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# PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON THE ANALYSIS AND DETECTION OF EXPLOSIVES



FBI ACADEMY  
QUANTICO, VIRGINIA  
MARCH 20-31, 1983

BEST COPY AVAILABLE

**Proceedings  
of the  
International Symposium  
on the  
Analysis and Detection of Explosives**

**MARCH 29-31, 1983  
FBI ACADEMY  
QUANTICO, VIRGINIA**

**Sponsored by The Federal Bureau of Investigation**



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Cover: Aerial photograph of FBI Academy by George February.

## Foreword

On March 29-31, 1983, the FBI hosted the "International Symposium on the Analysis and Detection of Explosives" in the Bureau's Forensic Science Research and Training Center at the FBI Academy at Quantico, Virginia. The Symposium was attended by 175 people from academia, Federal, state and local law enforcement forensic laboratories, the military and the explosives industry.

The 57 papers presented, covering all aspects of current R&D in the field of explosive analysis and detection, represented many new and interesting techniques.

This symposium was an outgrowth from the need to bring together scientists in the field who share common interests and problems in explosive analysis and detection for the purpose of enhancing dialog in the overall goal of controlling the use of explosives by terrorists and other criminals. The FBI is deeply appreciative that so many organizations and agencies were willing to share their expertise to help tackle a problem of international proportions.

I have received many comments on the level of professionalism and high standards of the meeting and its significance to the field of analytical chemistry. Indeed, these proceedings which are a compilation of the 57 papers presented, represent a milestone in the field.

On behalf of the FBI Laboratory, I would like to personally extend my thanks to the program committee, the individuals who presented papers and the other participants for making the Symposium what I believe was an overwhelming success.

JAMES H. GEER  
*Assistant Director  
in Charge*  
FBI Laboratory

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## KEYNOTE ADDRESS

### NEW HORIZONS IN MASS SPECTROMETRY FOR THE ANALYSIS OF EXPLOSIVES

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Rehovot, Israel

Mr. Chairman, Ladies and Gentlemen:

First, I would like to thank our host, the Federal Bureau of Investigation, and in particular the organizing committee, for the initiative and the organization of this important symposium; and, I would like to express my deep appreciation for being invited as the keynote speaker.

This meeting is important because it presents a unique forum where scientists from around the world are able to present, to listen to, and to discuss new approaches, new applications, new methods and new instrumentation in the field of analysis and detection of explosives.

Having seen the number of papers in the program and their topics, I believe that this meeting will be another milestone in this one area of the battle against crime and terrorism.

Our efforts should be concentrated toward the common goal of creating an international collaboration in this field. Exchange of information involving all scientists active in the analysis and detection of explosives is vital to the successful achievement of this goal.

The subjects of this collaborative effort should include the development of new instrumental methods and their evaluation; the improvement of established techniques; and the evaluation—for the analysis of explosives—of new techniques which have already proved to be successful in other fields. A typical example of this last group has been the introduction of chemical ionization mass spectrometry for the analysis of explosives, about 9 years ago, which was the result of a collaborative effort between our laboratory at the Weizmann Institute of Science and the Israeli Police.

Several new developments in mass spectrometry have appeared during the last few years and have been very successful in various analytical applications. These are:

- (1) On-line high performance liquid chromatography—mass spectrometry (LC/MS).
- (2) On-Line micro liquid chromatography—mass spectrometry (Micro LC/MS).
- (3) Tandem mass spectrometry (MS/MS).
- (4) Several novel ionization techniques:
  - (a) Laser desorption (LD).
  - (b) Fast atom bombardment (FAB).
  - (c) Secondary ion mass spectrometry (SIMS).

Initial experimentation with some of these techniques for the analysis of explosives has already been done, but a complete evaluation has still to be carried out.

I would like to describe one of these techniques: MS/MS, its principles, the instrumentation and possible applications in our field.

This technique has been pioneered by John Beynon [Bozorgzadeh, Morgan and Beynon (1978)] in the United Kingdom and by Fred McLafferty [Bente, III and McLafferty (1980)], Graham Cooks [Cooks and Glish (1981)] and Chris Enke [Yost and Enke (1979)] in the United States.

As can be understood from the technique's name, MS/MS, we are talking about the combination of two mass spectrometers. The combination of two techniques is well known from GC/MS and recently from LC/MS which consist of a combination of separation and identification techniques. MS/MS consists of two mass spectrometers in tandem with a reaction cell between them. A schematic illustration of an MS/MS is shown in Figure 1. The sample can be one single compound or a mixture. Accordingly we would use either electron impact (EI) or chemical ionization (CI) or any other ionization method.

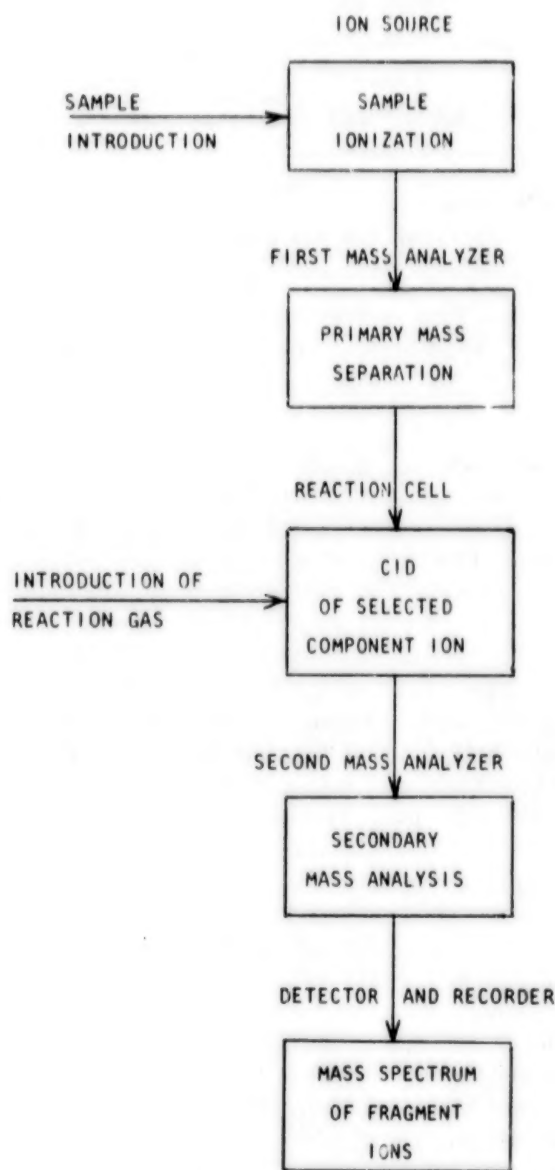


Figure 1. Schematic illustration of an MS/MS system.

The first mass analyzer separates the ions produced in the source. We select the primary ion to enter the reaction cell. For example, if the sample is a mixture, we will chose the  $MH^+$  ion of one of the components to enter the reaction cell. In the cell the primary ion beam collides with an inert gas such as helium, argon or nitrogen, resulting in collision-induced dissociation (CID) of the selected ion. This is also called collisionally activated dissociation (CAD).

There are two types of CID in the reaction cell, depending on the type of the first mass analyzer:

- (1) High-energy collisions if the first mass analyzer is a magnetic sector one. The primary ion has an energy of several KeV.
- (2) Low-energy collisions if the first mass analyzer is a quadrupole. The primary ion has an energy of 0–100 eV.

While in high-energy CID, the collisions of the ion with the inert gas transforms some of the translational energy of the ion into internal excitation energy, in low energy CID, the transfer of momentum plays a more important role than the transfer of energy; therefore larger molecules such as nitrogen are more effective than small atomic species such as helium, as collision gas.

The fragment ions produced in the reaction cell are mass analyzed by the second mass analyzer and recorded. This secondary mass spectrum provides a "fingerprint" of the primary ion beam.

There are several types of MS/MS configurations:

- (1) Reversed-geometry double-focusing mass spectrometer (CID-MIKES).
- (2) Triple quadrupole system.
- (3) Magnetic sector (B) and quadrupole (Q) combination (hybrid):
  - (a) BQQ
  - (b) QQB
- (4) Triple sector combination:
  - (a) BEQQ
  - (b) EBQQ
  - (c) BEB
- (5) Four sector combination, which includes two magnetic sector analyzers (B) and two electrostatic analyzers (E).

The reversed geometry double-focusing mass spectrometer uses the magnetic field as the first mass analyzer and the electrostatic analyzer as second mass analyzer. This particular configuration is called MIKES: mass analyzed ion kinetic energy spectrometry; because mass selection (by momentum analysis) is followed by an ion kinetic energy analysis of the product ions. The mass scale of the fragment ions formed in a MIKE spectrum is a linear function of the electric sector voltage. Figure 2 shows schematically the ion optical system of such a spectrometer.

The triple quadrupole system, Figure 3, consists basically of a tandem quadrupole mass spectrometer (first and third quadrupoles). The second quadrupole has only an R.F. voltage (without D.C. voltage) and serves therefore only as an ion focusing device. The reaction cell is located between the rods of this quadrupole. It has been found that when using a quadrupole mass analyzer, an additional quadrupole focusing device is needed to focus the ions in the reaction cell. This is also necessary in hybrid combinations.

In the triple quadrupole system the collisions of the primary ions with the neutrals are low energy collisions (0-100 eV). Figure 4 shows an example of a BEQQ triple sector system. This system has several reaction cells (collision cells) in different parts of the instrument, thus enabling a variety of experiments. Collision cell 2, between the magnetic and electrostatic analyzers is suitable for high energy CID, while collision cell 3, after the deceleration lens, is suitable for low energy CID experiments.

Several experiments can be carried out with an MS/MS:

- (1) Daughter experiment: allows a survey of specific compounds in complex organic mixtures. Each component of the mixture is represented by its molecular ion (in EI) or by its  $MH^+$  ion (in CI). Each of these chosen ions undergoes CID in the reaction cell and is identified by its CID mass spectrum at the collector of the second mass analyzer.

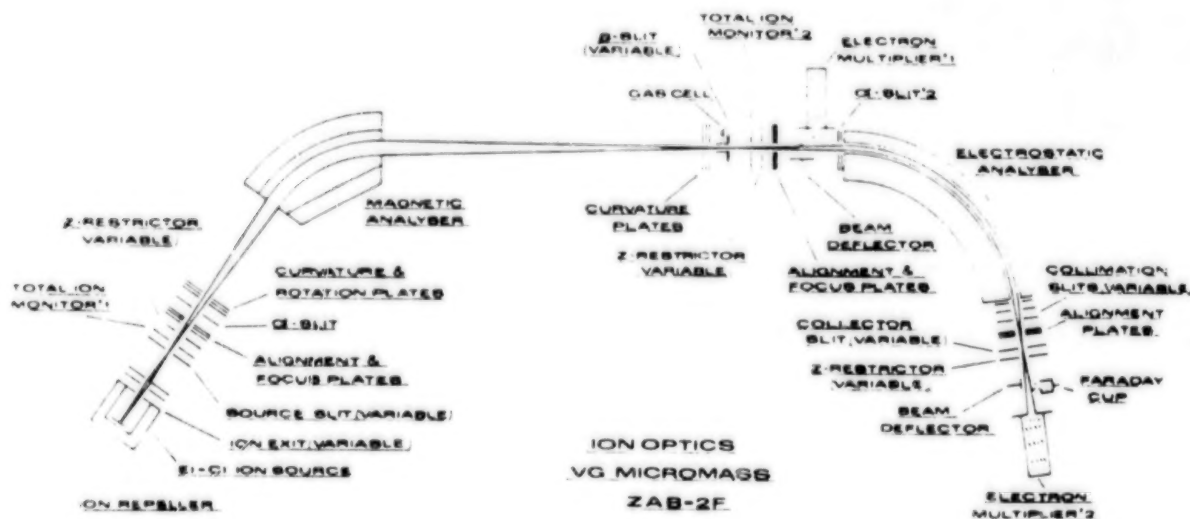


Figure 2. Ion optical system of a MIKE-CID spectrometer [Morgan *et al.* 1978].

## CUTAWAY VIEW OF TRIPLE QUADRUPOLE MS/MS SYSTEM

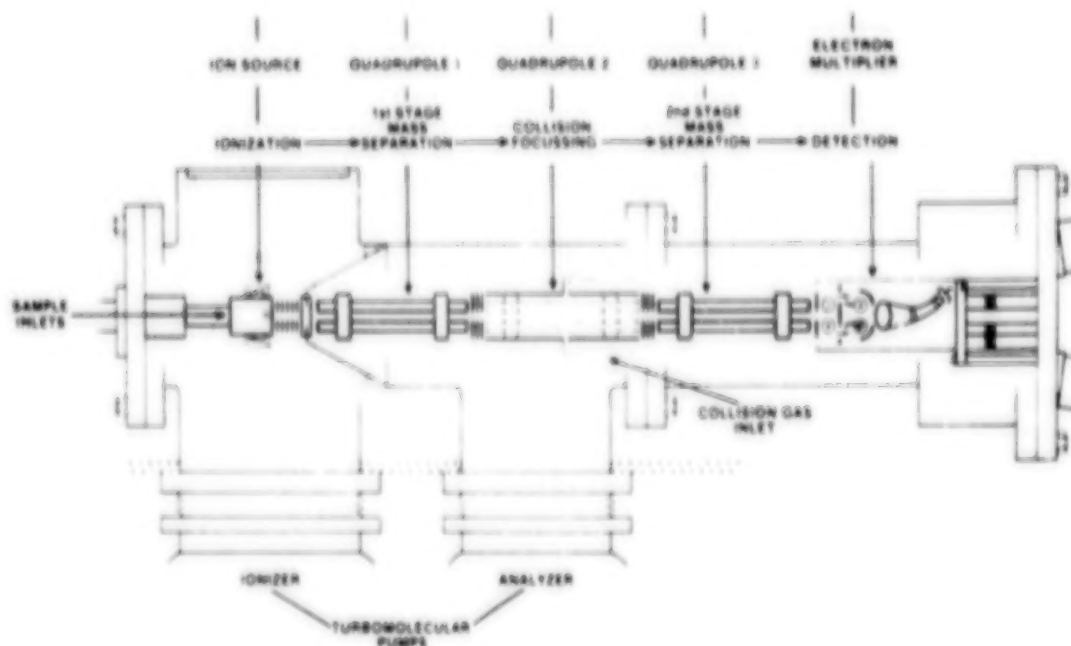


Figure 3. Triple quadrupole system [Slyaback and Story (1981)]

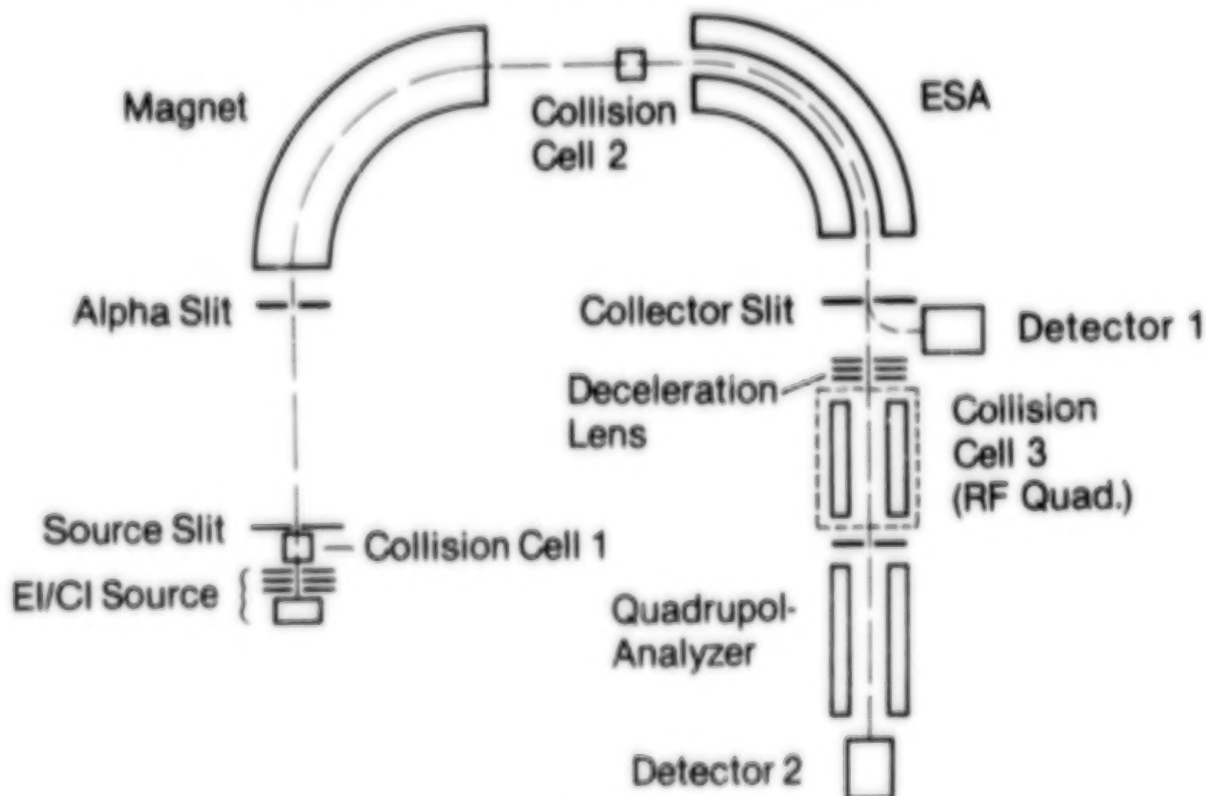


Figure 4. BEQQ triple sector system [Finnigan MAT (1982)]

(2) Parent experiment: the first mass spectrometer is scanned while the second is set at a specific mass. This experiment identifies all parent ions that decompose to a predetermined daughter ion which is being detected by the second mass spectrometer. This experiment will detect all compounds that decompose to a common fragment. For example, trinitroaromatic compounds could be identified by the  $\text{NO}^+$  fragment ion, while nitrate esters by the  $\text{NO}_2^+$  fragment ion.

(3) Neutral loss experiment: the mass analyzers are set to detect a constant neutral loss. For example, the first mass analyzer is scanned from  $m/z$  37 to 300, at the same time as the second mass analyzer is scanned from  $m/z$  20 to 283. In this example the neutral loss of 17 units may represent a series of nitrocompounds losing OH. In a similar way one might want to look for compounds which have a neutral loss of NO or  $\text{NO}_2$ . Neutral loss experiments can be done in a much easier way on a triple quadrupole instrument because quadrupoles are more suited for computer control.

Another use of MS/MS is structure identification and determination of fragmentation patterns. Fragmentation patterns of RDX and HMX have been determined by MS/MS using a MIKE-CID spectrometer [Yinon, Harvan and Hass (1982)]. It is well known that the mass spectrometry of RDX and HMX poses some problems [Yinon (1982)], because a whole series of fragment ions are produced even in the CI mass spectra. The origin of many of these fragments was difficult to explain, and therefore it was difficult to determine fragmentation patterns. The CID mass spectrum is related to the primary ion structure (or precursor ion structure) in the same way as the EI mass spectrum is related to the molecular structure. Hence the similarity between CID and EI spectra.

Figure 5 shows the MIKE-CID spectrum of the  $\text{MH}^+$  ion at  $m/z$  297 in HMX in the CI mode using methane as reagent gas. Such spectra were recorded for almost all the ions of RDX and HMX in EI, CI

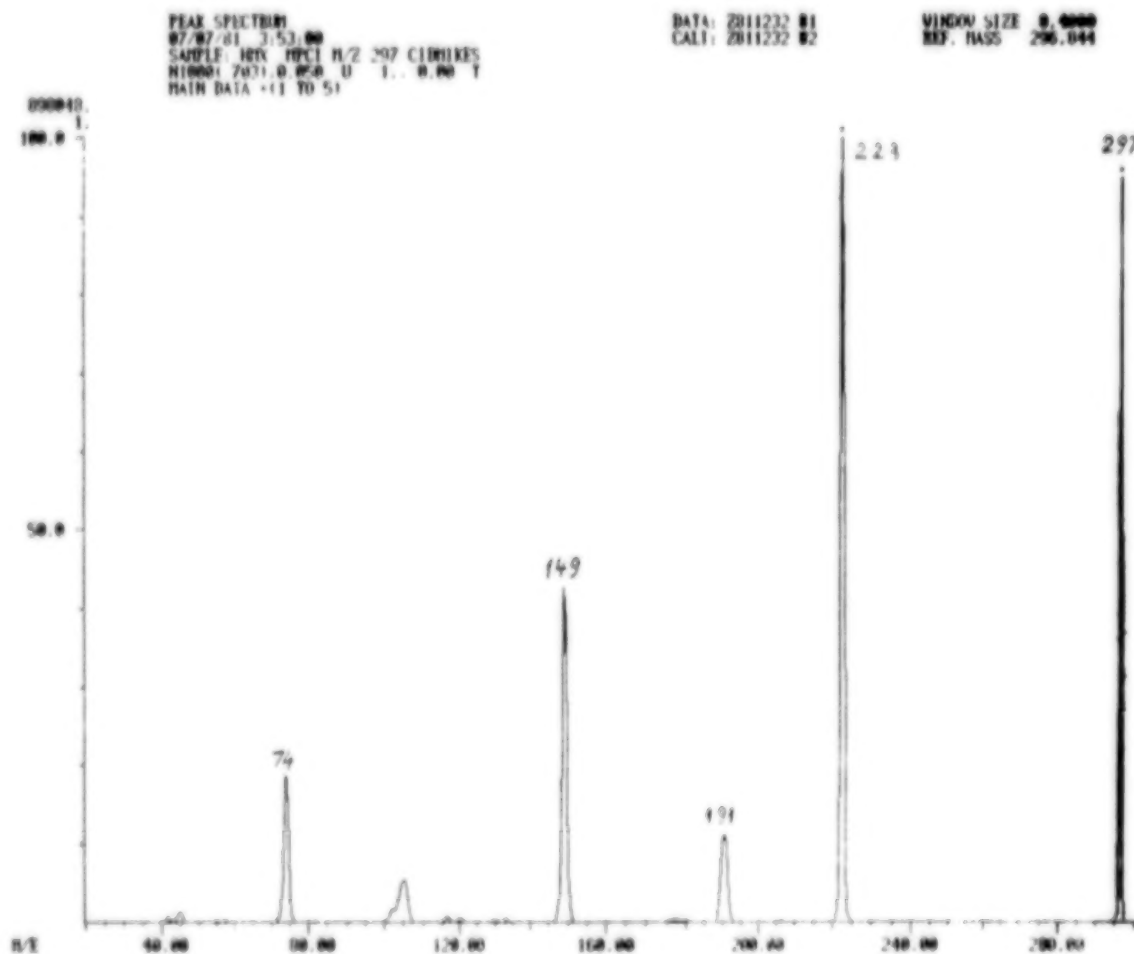


Figure 5. MIKE-CID spectrum of the  $\text{MH}^+$  ion at  $m/z$  297 in HMX in the CI mode with methane.



and negative-ion  $\text{Cl}^-$ . Fragmentation maps, like the one shown in Figure 6, were obtained. It was found that the adduct ions  $(\text{M} + \text{NO})^+$  and  $(\text{M} + \text{NO}_2)^+$  are the precursors of a large number of the fragment ions observed in the mass spectra of RDX and HMX.

Although MS/MS has been applied to a variety of analytical fields [Henion *et al.* (1982), Bateman *et al.* (1982), Hunt *et al.* (1982)], it has not yet been applied to the analysis of explosives.

The main features of MS/MS are: specificity, sensitivity and fast response. Therefore, the uses of this technique in residue analysis and detection of explosives seem obvious:

In residue analysis we might want to use one of the larger instruments, for example a hybrid one, with medium resolution, for the identification of explosive residues in debris. We would do either parent or daughter experiments. For detection of hidden explosives we would use a small computer controlled triple quadrupole system having a high pressure source or some molecular separation device which would enable the monitoring of large amounts of air. We would program such an MS/MS to do either a parent experiment to monitor fragment ions specific to explosives or to monitor neutral losses specific to explosives.

Those who have the instrumental know-how and the appropriate facilities can mount their own MS/MS instruments. Others can buy them, they are already commercially available; but they are very expensive. The British writer Samuel Butler said already, about a century ago: "Though wisdom cannot be gotten for gold, still less can it be gotten without it". The need for money in research is not new, and today more than before: as analytical instrumentation becomes more sophisticated, it becomes more expensive. Therefore, collaboration becomes more and more important. I believe that we should try to increase the interest of scientists from the academic world in our subjects, especially those who are using novel analytical techniques; and we should increase international collaboration in order to avoid duplication of efforts and to enhance research and development.

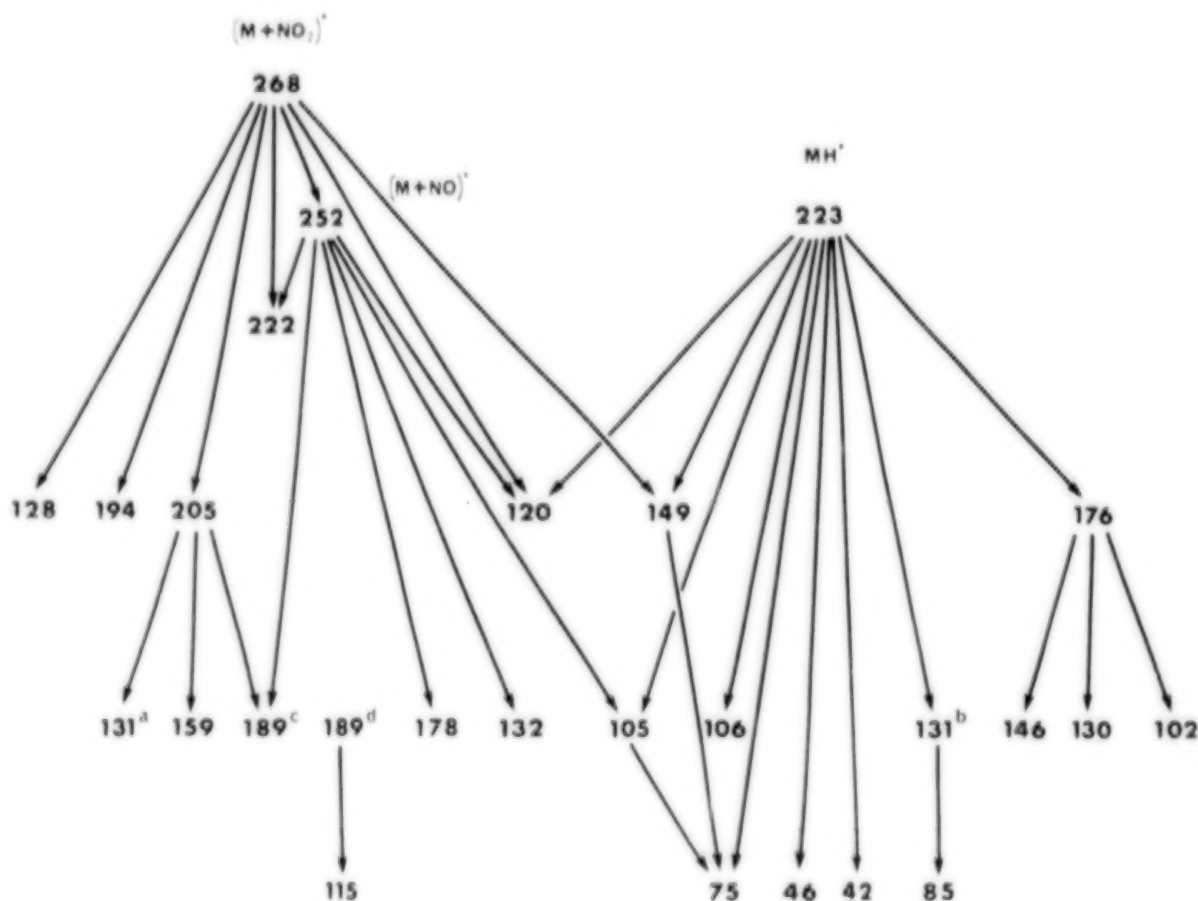


Figure 6. Fragmentation map of RDX in the CI mode [Yinon *et al.* (1982)].

Finally, let me take this opportunity to make two suggestions which, I think, should be discussed during the following few days:

First, to establish an association or society. The field of analysis and detection of explosives has always been a small subdivision of forensic sciences or other disciplines. I believe that this field has now become, because of its importance, an independent field. So now is the time to create an International Association for the Analysis and Detection of Explosives.

The second suggestion is to establish that these International Symposia be held on a permanent basis every 3 years and in a different country. I propose to host the next symposium in 3 years at the Weizmann Institute of Science in Rehovot, Israel.

I believe that the establishment of an association, together with periodical symposia, will bring more people in the field of analysis and detection of explosives and will increase large scale collaboration.

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**SYMPOSIUM PRESENTATIONS**

**HIGH PERFORMANCE LIQUID  
CHROMATOGRAPHY METHODS**

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# THE TRACE ANALYSIS FOR EXPLOSIVES AND RELATED COMPOUNDS VIA LIQUID CHROMATOGRAPHY-ELECTROCHEMISTRY (LCEC)

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**ABSTRACT.** Although explosives and related organic nitro compounds have now been analyzed *via* reductive liquid chromatography-electrochemistry (LCEC) methods, it is generally acknowledged that oxidative LCEC could not be at all compatible with this class of compounds. That is, organic nitro derivatives are already in their highest oxidation state, and thus could not readily be detected *via* oxidative LCEC. We have now developed a post-column, on-line, real-time photolysis/derivatization approach that generates inorganic nitrite from virtually all explosives and organic nitro compounds after these elute from the analytical high performance liquid chromatography (HPLC) column. This inorganic nitrite is then detected *via* conventional thin-layer flow-through electrode detection in LCEC, using single and dual cells in the oxidative and/or reductive modes. These newer methods of trace analysis for explosives have now been applied to mixtures of such standards, nitroaromatics, nitro polycyclic aromatic hydrocarbons, nitro drugs, organic nitrate esters, and related nitro derivatives. We have determined calibration plots for a large number of explosives using flow injection analysis, photolysis-EC, as well as HPLC-photolysis-EC (HPLC-hv-EC) methods. At the same time, we have determined minimum detection limits (MDLs) for a large number of these compounds, suitable HPLC separation conditions using reversed phase methods, and have utilized dual electrode response ratioing in order to improve analyte identification. At the same time, it has been possible to apply these overall methods of analysis to certain real world samples of post-blast debris extracts, wherein the selectivity and specificity of the overall HPLC-hv-EC methods are readily and fully demonstrated. It is suggested that these trace organic analysis approaches for explosives should be readily adaptable and applicable to a large number of other real-world samples in other laboratories.

## INTRODUCTION [1]

Most commonly used explosives contain the nitro ( $\text{NO}_2$ ) group somewhere within their structures, usually bonded directly to either carbon, nitrogen, or oxygen atoms ( $\text{C-NO}_2$ ,  $\text{N-NO}_2$ , or  $\text{O-NO}_2$ ). Indeed, most explosives contain more than one nitro group per molecule of the compounds. Although most of the early work on the

analysis of explosive materials utilized gas chromatography (GC), with a wide variety of suitable and often selective/sensitive detectors, within the past decade or so, much of the emphasis in such analyses has shifted towards the utilization of high performance liquid chromatography [Yinon (1977), Yinon and Zitrin (1981), Krull and Camp (1980), Krull (1983), Krull *et al.* (1981), Bratin *et al.* (1981), Alm *et al.* (1978), FBI Academy Sym-

posium (1983)]. Already, a large number of selective or general type detectors for HPLC have been shown to be suitable for the trace analysis of complex mixtures of explosives, including: ultraviolet-visible (UV-VIS); electron capture detection (ECD); mass spectrometry (MS); Thermal Energy Analysis (TEA); reductive electrochemical detection (EC); and others. However, there remain certain quite significant disadvantages inherent within each of these detection approaches. Thus, UV-VIS is often not selective enough for explosives alone, and it is not generally sensitive enough either; ECD is no longer commercially available, and it is not easily compatible with reversed phase HPLC solvents; MS can be used as an LC detector, but it tends to be very expensive, difficult to operate routinely, and requires sophisticated operator training and/or experience; TEA is somewhat selective for organic nitro compounds, but it will respond to other classes, it is not at all compatible with aqueous based reversed phase HPLC separations, and it is very expensive as a routine HPLC detector goes; and finally, reductive EC has only been utilized by very few workers thus far. Reductive EC can, at times, present serious operational problems, especially at the trace levels of analysis, where oxygen in the sample and mobile phase can interfere with the analyte of interest. However, it is clear today that reductive LCEC is becoming more and more popular and routinely used as a method of trace organic/inorganic analysis, and thus it may yet become a method of choice for various explosives and organic nitro compounds. Still, at the present time, oxidative liquid chromatography-electrochemistry (LCEC) or HPLC-EC is the more widely used and preferred mode of electrochemical detection in HPLC [Krull *et al.* (1983a), Shoup *et al.* (1982), Krull *et al.* (1983b), Roston *et al.* (1982)]. Clearly, nitro derivatives, such as the explosives studied here, are not directly amenable to oxidative LCEC approaches, since they are already in their highest oxidation state. However, there was sufficient evidence and encouragement in the literature to indicate the possibility of using oxidative LCEC for inorganic nitrite ( $\text{NO}_2^-$ ), perhaps generated on-line, post-column, in real-time, from suitable precursor organic nitro compounds [Krull and Lankmayr (1982), Lefevre *et al.* (1982), Snider and Johnson (1979), Sherwood and Johnson (1981), Scholten *et al.* (1980), Green *et al.* (1977), Iwaoka and Tannenbaum (1976), Fogg *et al.* (1982)].

Oxidative LCEC has long been used for the trace determination of inorganic nitrite, using ion chromatography, ion exchange HPLC, or paired-ion HPLC [Davenport and Johnson (1974), Molnar *et al.* (1980), Stevenson and Harrison (1981), Bratin (1981)]. Thus, there was little question that nitrite was indeed amenable to oxidative LCEC approaches, with working potentials of +1.2V or below, and that dual electrode EC detection was another approach that could eventually be utilized for explosives. The overall success of this newer approach for explosives therefore relied on the release of inorganic nitrite from suitable organic nitro derivatives, perhaps *via* a photohydrolysis/photolysis type reaction for derivatization, after the HPLC separation step before the oxidative EC detection step(s). Most of the literature utilizing photohydrolysis derivatizations in HPLC have involved the formation of nitrite from various N-nitroso compounds, followed by analysis of the nitrite by a Griess Test or alternative HPLC detection methods [Snider and Johnson (1979), Sherwood and Johnson (1981), Scholten *et al.* (1980), Green *et al.* (1977), Iwaoka and Tannenbaum (1976)]. In essence, the photoconductivity detector for HPLC now marketed by Tracor Corporation (Austin, Texas) involves photolysis/photohydrolysis reactions on various organic compounds, including N-nitroso or organohalogens, followed by detection of the inorganic anions once formed *via* an on-line conductivity detector [Popovich *et al.* (1979), McKinley (1981)]. In almost all of this work yet described with on-line, real-time, photohydrolysis reactions leading to the formation of inorganic anions, virtually nothing had been done emphasizing organic nitro compounds. There has been a suggestion in the work of Snider and Johnson in the use of a photoelectroanalyzer for N-nitroso compounds, that organic nitro compounds were often seen as interferents in the primary analysis. That is, at least some nitro derivatives were shown to lead to the presumed formation of nitrite *via* a photohydrolysis reaction, after the HPLC separation, and this could then lead to a false positive in the direct analysis for N-nitroso compounds [Snider and Johnson (1979)]. However, nothing further was ever described or discussed in this work or that of others using photohydrolysis or photolysis in HPLC determinations of N-nitroso compounds. Nevertheless, all of the available literature seemed to strongly suggest that HPLC-photolysis-EC (HPLC-hv-EC) might very well serve

as a useful and practical approach for the trace analysis and speciation of a wide variety of explosives and other organic nitro compounds/analytes. At the same time, these methods could be adapted to other classes of organic compounds, wherein these can release an inorganic anion *via* photolysis that could then be detected by EC means.

Although our initial interest in the use of HPLC-hv-EC was directed to the trace analysis of explosives, it rapidly became apparent that these basic methods could just as readily be used with a wide variety of other organic nitro compounds, besides explosives. We therefore describe here our overall analytical results for a variety of commonly used explosives, including: 2,4,6-trinitrotoluene (TNT); dinitrotoluene (DNT); nitroglycerin (NG); 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX); 2,4,6,N-tetranitro-N-methylaniline (TETRYL). In addition, we have applied HPLC-hv-EC to certain simple aliphatic nitrate esters (R-O-NO<sub>2</sub>), such as *n*-propyl nitrate and isopropyl nitrate, as well as to a particular coronary vasodilator, isosorbide dinitrate (ISDN). Finally, we have tried to apply these analytical methods to various aromatic nitro derivatives, such as mono-nitrotoluene isomers, dinitrotoluene isomers, and certain nitro derivatives of polycyclic aromatic hydrocarbons (nitro-PAHs). We have also attempted to define what inorganic anions might interfere in these HPLC-hv-EC analyses for organic nitro compounds, and which inorganic anions present no potential problems as interferents. Indeed, these results suggest that there will be several other classes of organic compounds that will be shown to produce significant responses in HPLC-hv-EC approaches. Improved analyte identification and compound specificity is possible *via* the use of appropriate dual electrode EC approaches, wherein these are feasible/practical for the particular inorganic/organic anion generated by the photolysis/photohydrolysis reaction. In addition, these results are shown to provide a flow injection analysis method, in the absence of an initial HPLC separation, utilizing just hv-EC, that can/could be practical for quality control or screening purposes.

## EXPERIMENTAL PROCEDURES

### Reagents, Chemicals, and Explosives Standards

Figure 1 illustrates some of the explosives studied here *via* HPLC-hv-EC and hv-EC approaches. Standards of these compounds were ob-

tained from the Bureau of Alcohol, Tobacco, and Firearms (U.S. Treasury Department) Forensic Laboratory, Rockville, Maryland, *via* the assistance and cooperation of Mr. A. Cantu. Some of these explosives were obtained from the FBI Academy, Forensic Research and Training Center, Quantico, Virginia, *via* the assistance of Dr. T. Rudolph. Two samples of post-blast debris extracts were also obtained from the above ATF laboratory, with the cooperation of Mr. Rick Strobel. Such samples were received as acetonitrile solutions, and were analyzed by direct injection onto HPLC-hv-EC, as below. These particular samples had been analyzed at the ATF by thin-layer chromatographic methods and were found to contain NG. A nitroglycerin standard was a sample of Parke-Davis Nitrostat-IV, lot AK725, 8mg/ml infusion solution, available as a prescription drug for heart ailments. Other organic nitro standards were obtained from commercial sources, such as: Aldrich Chemical Co. (Milwaukee, Wisc.), Pfaltz & Bauer Co. (Stanford, Conn.), or Fisher Scientific Co. (Medford, Mass.). Inorganic salts were obtained from a variety of commercial

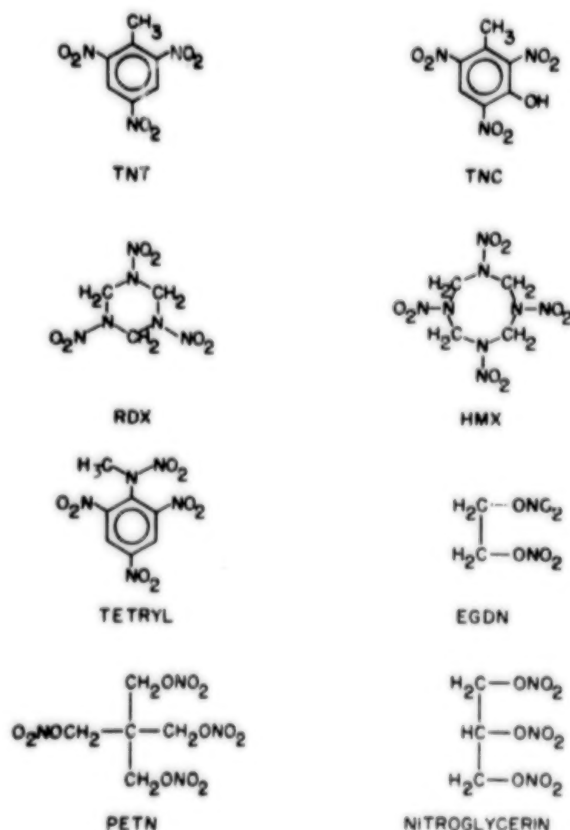


Figure 1. Structures of some of the more commonly used explosives.

sources, including: J. T. Baker Chemical Co. (Phillipsburg, N.J.), Fisher Scientific Co., Aldrich Chemical Co., and others. The HPLC Solvents, especially water (HOH) and methanol (MeOH), were obtained from Waters Assocs., Inc. (Milford, Mass.) or MCB Chemicals Co. (Cincinnati, Ohio), the latter as their Omnisolv brand of HPLC grade solvents.

### Instrumentation and Equipment

Figure 2 illustrates the overall HPLC-hv-EC instrumentation used in all of these studies, and the orientation/arrangement of the various parts of the analytical system. The HPLC portion in Figure 2 utilized a Rheodyne Model 7125 syringe loading injection valve (Rheodyne Corp., Cotati, Calif.), a Laboratory Data Control (LDC) Constametric II solvent delivery system (Laboratory Data Control, Riviera Beach, Fla.), a LiChroma-Damp II pulse dampener (Alltech Assocs., Inc., Deerfield, Ill.), a Bioanalytical Systems pulse dampening column (Bioanalytical Systems, Inc., West Lafayette, Ind.), a Photronix Model 816 HPLC batch irradiator (Photronix Corp., Medway, Mass.), a BAS Model LC-4A single electrode amperometric controller or a BAS Model LC-4B dual electrode amperometric system for HPLC/LCEC, a BAS glassy carbon single or dual working electrode with a Ag/AgCl reference electrode, and finally, a Linear Instruments Model 585 dual pen strip chart recorder (Linear Instruments, Inc., Reno, Nevada). All HPLC injections were made with a 25ul flat-tipped Hamilton HPLC syringe (Hamilton Corp., Reno, Nevada). HPLC mobile phases were de-gassed and filtered prior to use via a 0.45um solvent filtration kit (Millipore Corp., Bedford, Mass.). Samples for HPLC injection were initially filtered with a sam-

ple filtration kit using a 0.45um filter (Millipore Corp.). The irradiation finger, Figure 2, was maintained at a constant temperature of about 0-5°C, with a constant temperature water bath (Forma Scientific, Model 2095, VWR Scientific Co., Boston, Mass.). Irradiation of the HPLC eluents took place inside a 10-12', 1/16" o.d., 0.030" i.d., Teflon FEP tubing, catalog no. HGC-024 (Rainin Instruments Co., Woburn, Mass.). Swagelok stainless steel fittings and ferrules were used for all of the HPLC-hv-EC connections, except wherein the EC detector cells required their own, already present connection fittings (Cambridge Valve & Fittings Co., Billerica, Mass.). The dual electrode HPLC-hv-EC unit utilized HPLC-hv-EC equipment/instrumentation similar to that described above for the single electrode unit, replacing the single electrode amperometric controller with the dual electrode/controller system from BAS. In the reductive mode of detection, the HPLC mobile phase was first de-gassed under nitrogen using an approach already described elsewhere [Bratir *et al.* (1981), Krull *et al.* (1983a), Krull *et al.* (1983b)]. The use of a Teflon irradiation line before the EC detector in the reductive mode of LCEC did not preclude the ability to perform trace explosives analyses at moderate working potentials, as below. The HPLC columns utilized in these studies were obtained from a variety of sources, including: 1) Biophase C<sub>18</sub>, 10um, 25-cm x 4.6-mm i.d. (Bioanalytical Systems, Inc.); 2) A Perkin-Elmer Fast-LC C<sub>18</sub>, 3um, 10-cm x 4.6-mm i.d. (Perkin-Elmer Corp., Norwalk, Conn.); 3) a Waters uBondapak C<sub>18</sub>, 10um, 25-cm x 4.6-mm i.d. (Waters Associates); and 4) various in-house slurry packed C<sub>8</sub> or C<sub>18</sub> reversed phase columns.

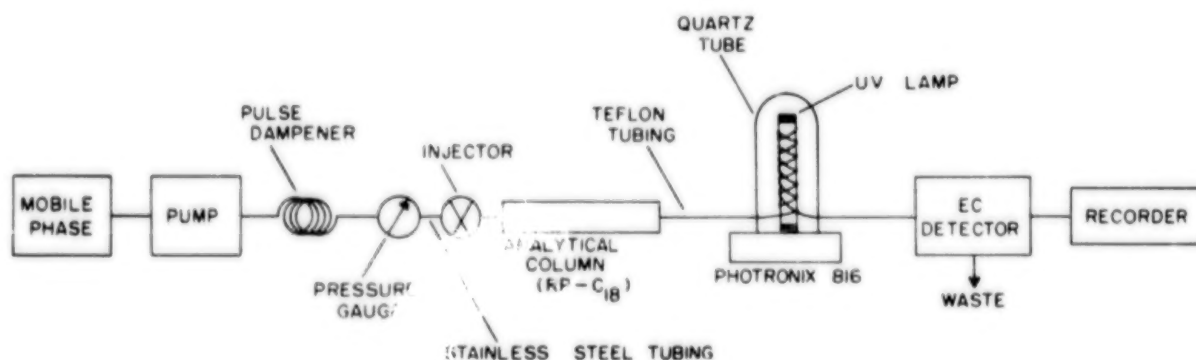


Figure 2. Schematic diagram of an on-line approach for performing nitro compound and explosives analysis via reversed phase HPLC with photohydrolytic derivatization after the analytical column via UV lamp irradiation of analytes, followed by oxidative/oxidative EC detection of nitrite generated in photolysis step of overall HPLC-hv-EC analysis.



## Methods and System Optimization

The cyclic voltammograms (CV) were obtained on a Bioanalytical Systems Model CV-1B unit, using a supporting electrolyte of 50/50 MeOH/0.1M NaCl, with a scan rate of 150mV/sec, with a Ag/AgCl reference electrode and a glassy carbon working electrode. The CVs were obtained by plotting applied working potentials vs current generated/observed, in the conventional, standard approach.

The final hv-EC and HPLC-hv-EC systems had to be optimized before their use with either standard mixtures of explosives or real world samples, and this was crucial for the photochemical irradiator/reactor part of the overall system, Figure 2. This was accomplished by varying both the internal diameter of the Teflon tubing and its total length wrapped around the irradiator finger. By measuring EC peak heights or current generated as a function of either the i.d. or total length, for the same concentration of explosives injected with hv-EC methods, it was then possible to determine the optimum tubing parameters that would provide maximum nitrite generation with minimum nitrite destruction from the various explosives of interest here. An external standard of nitrite was used, with the lamp off, as a control to determine optimization of nitrite generated from the explosives with the lamp on in the hv-EC approaches. The optimal flow rate was then determined also *via* flow injection methods (hv-EC), without the HPLC column on-line, again using the maximum nitrite generated from various nitro compounds or explosives. This suggested ideal flow rates and residence times for the final HPLC-hv-EC system. The hv-EC system also had to be optimized with regard to salt concentration and which salts were compatible with both photolysis and EC detector conditions. A number of conventional inorganic salts were studied in these regards, but only NaCl appeared to be totally inert to the photolysis and EC conditions, and to be free of impurities that might interfere in the final hv-EC analyses. The effect of pH also had to be optimized for hv-EC approaches, and again this was accomplished by using maximum nitrite generated from the same standards (nitro compounds) to indicate ideal pH values that could then be used in the final HPLC-hv-EC studies. All of the final operating parameters, as below and in various Figures that follow, were then utilized for both the flow injection studies (hv-EC) and the HPLC-hv-EC analyses of various standard mixtures of explosives and real world, post-blast extract samples.

## RESULTS AND DISCUSSION

### Initial Cyclic Voltammogram Studies for Inorganic Anions, Possible Interferents in hv-EC and HPLC-hv-EC for Trace Analysis of Explosives and Nitro Compounds

These HPLC-hv-EC or flow injection analysis *via* hv-EC methods depend initially on the photolytic or photohydrolytic generation of an inorganic or organic anion from an appropriate organic precursor for trace organic analysis. These needs are quite similar to those needed in photoconductivity detection in HPLC trace organic analysis. It is also possible that certain inorganic anions, electrochemically active in the absence of any photolysis, might be converted *via* photolysis to electrochemically active species/ions. Thus, these basic approaches may yet prove applicable for both organic and inorganic trace analyses, in addition to the applications described herein. In FIA (hv-EC) approaches, there may often be a problem of interferences arising in the direct analysis of an explosive compound or organic nitro material, by one or more inorganic/organic anions already present in the same sample matrix/solution. In order to determine such possible interferents, we obtained a series of cyclic voltammograms (CV) for four typical inorganic anions of interest as possible interferents or photolysis products derived from suitable organic precursors, Figure 3. Of the four inorganic anions of most interest for final HPLC-hv-EC applications, it is quite clear that nitrate ( $\text{NO}_3^-$ ) is not oxidized at the potentials of interest in EC detection. At the same time, Figure 3 indicates that nitrite ( $\text{NO}_2^-$ ), iodide ( $\text{I}^-$ ), and bromide ( $\text{Br}^-$ ) all have very different optimal oxidation potentials for maximum current generated in either CV or EC detection. Hence, it should be readily possible to differentiate between an organic nitrate ester, an aromatic C-nitro derivative, an organic alkyl nitrite ( $\text{R-O-NO}$ ), an organoiodine ( $\text{R-I}$ ) compound, an organobromine ( $\text{R-Br}$ ) substance, each of these leading to the corresponding anions *via* photolytic derivatization (i.e.,  $\text{NO}_3^-/\text{NO}_2^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}/\text{NO}_2^-$ ,  $\text{I}^-$ , or  $\text{Br}^-$ ). However, an organic nitrate ester ( $\text{R-O-NO}_2$ ) could conceivably lead to both nitrite and nitrate on irradiation, while an aromatic nitro compound or an alkyl C-nitro material might only lead to inorganic nitrite on irradiation. It is also possible that the initially formed nitrate or nitrite species could further react with oxygen in the aqueous based solution or HPLC mobile phase, leading to further/additional EC active species. It is also possi-



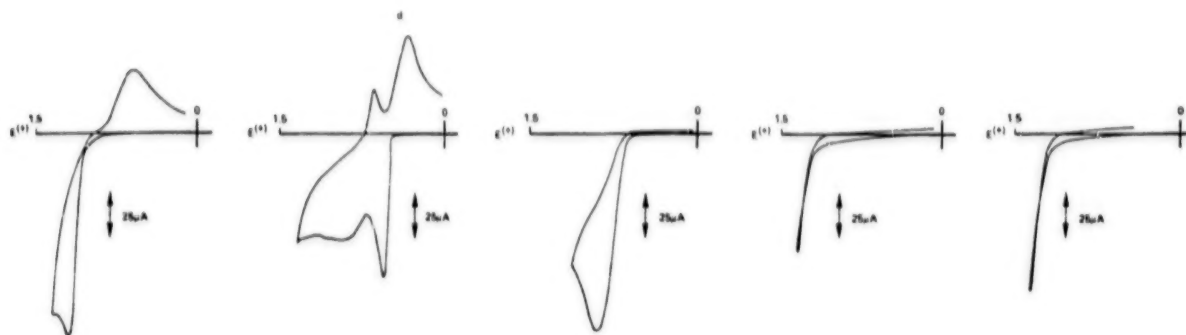


Figure 3. Cyclic voltammograms of various inorganic anions of interest in HPLC-hv-EC trace analysis for organic precursors leading to such anions by photolysis: a) supporting electrolyte of MeOH/0.1M NaCl (50/50, v/v); b) 0.0065M KNO<sub>3</sub>; c) 0.0048M NaNO<sub>2</sub>; d) 0.0026M KI; and e) 0.0035M KBr. All CVs performed at a glassy carbon electrode with scan rate of 150mV/sec, x-axis volts vs Ag/AgCl, y-axis in microamperes.

ble that other electroactive species, in addition to nitrate/nitrite, could be formed from certain organic nitro compounds on initial photolysis/irradiation. Our results support the already established fact that photolysis of organic nitrate esters and aromatic C-nitro compounds can lead to release of inorganic nitrite, and that this is then readily detected *via* oxidative EC methods [Binkley and Koholic (1979)]. Since inorganic nitrite was of most interest here as the major photolysis product derived from all of the explosives and nitrate esters studied here, we obtained a separate linear hydrodynamic voltammogram using flow injection analysis methods. This plot indicated usable oxidative working potentials for EC detection of nitrite of about +0.8 to +1.0V. Indeed, such working potentials for the analysis of nitrite had already been suggested in the existing literature [Sherwood and Johnson (1981), Davenport and Johnson (1974)]. Thus, for most of the studies that follow, especially in the HPLC-hv-EC work, we have tended to emphasize oxidative potentials around +1.0V, with either a glassy carbon single or dual working electrode system.

In order to further delineate which inorganic/organic anions might cause interferences in the hv-EC or HPLC-hv-EC analyses of explosives and organic nitro compounds, we determined the EC oxidative responses for a large number of such anions with and without the lamp/irradiator turned on, Table 1. These overall results suggest that there are relatively few inorganic or organic anions that produce the same qualitative results as does inorganic nitrite under these particular EC operating potentials/conditions. When quantitative values are obtained for the oxidative responses for nitrite at two different working potentials, and these are then compared with the same values for other anions that might be interferences in the analysis for nitrite, it is readily seen that only nitrite has a characteristic ratio of EC responses. Thus, the use of dual detector response ratioing in hv-EC or HPLC-hv-EC could/should provide almost unequivocal qualitative and quantitative fingerprints or handles for individual inorganic anions generated *via* photolysis from very specific organic precursors. Indeed, these initial speculations have now been confirmed, as below.

Table 1. SUMMARY OF POSSIBLE INORGANIC ANION RESPONSES IN HPLC-hv-EC USING hv-EC

Anion Studied	EC Active With Lamp Off		EC Active With Lamp On	
	+ 0.8 V	+ 1.0 V	+ 0.8 V	+ 1.0 V
Cl <sup>-</sup>	NO	NO	NO	NO
ClO <sub>2</sub> <sup>-</sup>	NO	NO	NO	NO
ClO <sub>4</sub> <sup>-</sup>	NO	NO	NO	NO
Br <sup>-</sup>	NO	NO	NO	NO
F <sup>-</sup>	NO	NO	NO	NO
I <sup>-</sup>	YES	YES	YES	YES
IO <sub>3</sub> <sup>-</sup>	NO	NO	YES	YES
IO <sub>4</sub> <sup>-</sup>	NO	NO	YES	YES
CO <sub>3</sub> <sup>-2</sup>	YES	YES	YES	YES
HCO <sub>3</sub> <sup>-</sup>	NO	NO	YES	YES
NO <sub>2</sub> <sup>-</sup>	YES	YES	YES	YES
NO <sub>3</sub> <sup>-</sup>	NO	NO	YES	YES

**Table 1. SUMMARY OF POSSIBLE INORGANIC ANION RESPONSES IN HPLC-hv-EC USING hv-EC—Cont.**

Anion Studied	EC Active With Lamp Off		EC Active With Lamp On	
	+ 0.8 V	+ 1.0 V	+ 0.8 V	+ 1.0 V
SO <sub>3</sub> <sup>-2</sup>	YES	YES	NO	NO
SO <sub>4</sub> <sup>-2</sup>	NO	NO	NO	NO
HSO <sub>3</sub> <sup>-</sup>	YES	YES	YES	YES
S <sup>-2</sup>	YES	YES	YES	YES
BENZOATE	NO	NO	YES	YES
ACETATE	NO	NO	NO	NO
CNS <sup>-</sup>	NO	YES	YES	YES
CN <sup>-</sup>	YES	YES	YES	NO
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	NO	NO	YES	YES
HPO <sub>4</sub> <sup>-</sup>	NO	NO	YES	YES
HPO <sub>2</sub> <sup>-</sup>	NO	NO	NO	NO
CrO <sub>4</sub> <sup>-2</sup>	NO	NO	NO	YES
Cr <sub>2</sub> O <sub>7</sub> <sup>-2</sup>	NO	NO	NO	YES
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>	NO	NO	NO	NO

a. These analyses of possible anion responses via dual electrode EC in hv-EC approaches were done using flow injection methods, with no HPLC column yet in-line. Dual electrode glassy carbon cell used here.

#### Qualitative EC Oxidative Responses for Explosives, Drugs, Aromatic Nitro Compounds, and Organic Nitrate Esters via Photolysis-EC (FIA) Methods

Knowing the optimum potentials for oxidative EC detection of the expected anions to be derived from explosives or other nitro compounds *via* hv-EC methods, it was then necessary to demonstrate that such analytes would indeed respond in flow injection analysis (FIA) under these irradiation conditions. At the same time, it was necessary to show that there would be no response on the EC detector for such compounds/substrates with the lamp off, Table 2. These studies were done after the hv-EC system had been optimized, as already described (Experimental Procedures). Of interest

here is the clear observation that inorganic nitrate does not show any response at these oxidative potentials with the lamp off, as expected, but that after irradiation, it does show a very good EC response at these same working potentials. This suggests that there may be some photoreduction of the nitrate to nitrite occurring, and that it is the final nitrite that is being detected in hv-EC or HPLC-hv-EC with the lamp turned on. It would appear, therefore, that FIA using hv-EC methods might provide a rapid, reliable, specific, sensitive, and quite reproducible method of direct analysis for these and other explosives and related organic nitro compounds. This would include nitro derivatives of various polycyclic aromatic hydrocarbons (PAHs), such as 9-nitroanthracene, Table 2. Such

**Table 2. DUAL ELECTRODE EC RESPONSES FOR VARIOUS EXPLOSIVES, NITRATE ESTERS, AROMATIC NITRO COMPOUNDS, DRUGS, AND RELATED COMPOUNDS VIA PHOTOLYSIS-ELECTROCHEMICAL DETECTION (hv-EC).**

Explosive or Nitro Compound	Compound EC Active With Lamp Off		Compound EC Active With Lamp On	
	+ 0.8V	+ 1.0V	+ 0.8V	+ 1.0V
TNT	NO	NO	YES	YES
RDX	NO	NO	YES	YES
TETRYL	NO	NO	YES	YES
NG	NO	NO	YES	YES
ISDN	NO	NO	YES	YES
iso-PROPYLNITRATE	NO	NO	YES	YES
n-PROPYLNITRATE	NO	NO	YES	YES
9-NITROANTHRACENE	NO	NO	YES	YES
o-NITROTOLUENE	NO	NO	YES	YES
DINITROBENZENE	NO	NO	YES	YES
DINITROTOLUENE	NO	NO	YES	YES
SODIUM NITRATE	NO	NO	YES	YES
SODIUM NITRITE	YES	YES	YES	YES

a. These determinations were performed *via* flow injection methods, with no HPLC column on-line, using just the basic photolysis-EC system (hv-EC).

compounds are of current widespread interest and concern as possible environmental pollutants having demonstrated animal/human carcinogenic and/or mutagenic properties and potentials. However, the use of FIA techniques for such analyses might only be feasible wherein the sample matrix is relatively simple, and/or wherein there would be very few, if any anionic interferents already present in the sample matrix that could produce similar dual electrode responses at these particular operating/working potentials used for organic nitro derivatives.

We have, in a separate, but related study, investigated the dual electrode response ratios at fixed concentrations injected for two different oxidative potentials, using various explosives and nitro derivatives, Table 3. These results were also obtained using flow injection methods, hv-EC, wherein the same concentrations of each analyte were injected under identical working/operating conditions. These overall results suggest that each and every individual explosive, drug, nitroaromatic, or nitro-PAH, may have its own unique dual detector response ratio. Such a quantitative characteristic for each analyte could then be used to further confirm its presence in a simple sample matrix *via* hv-EC (FIA) methods, or in more complex sample matrices, using HPLC-hv-EC approaches. That is, wherein an explosive is thought to be present in a real-world, post-blast extract sample, its presence could be more accurately confirmed using the dual detector response ratio for the analyte in the sample, and comparing this value with the corresponding value obtained for an authentic standard of the suspected explosive. This method has indeed now been applied to an actual, real-world explosion debris extract, as indicated below.

**Table 3. DUAL ELECTRODE RESPONSE RATIOS AT FIXED CONCENTRATIONS INJECTED FOR TWO DIFFERENT OXIDATIVE POTENTIALS, +1.0V/+0.8V, FOR VARIOUS EXPLOSIVES AND NITRO DERIVATIVES.<sup>a</sup>**

Compound Studied	Dual Electrode Response Ratios
NG	4.33
TETRYL	2.00
TNT	2.25
RDX	3.00
ISDN	1.64

a. These detector response ratios were determined *via* flow injection analysis, hv-EC, at the two working potentials of +1.0V and +0.8V. Ratios were calculated at the same concentration of each nitro derivative injected for plots of the detector responses at a number of concentrations injected at these two working electrode potentials. All hv-EC analyses were performed within the same working day.

#### Calibration Plots *via* hv-EC and Minimum Detection Limits for Various Explosives *via* HPLC-hv-EC Approaches/Methods

We have now obtained, *via* single and dual electrode EC methods, in hv-EC (FIA), a number of calibration plots and minimum detection limits for various explosives, aromatic nitro compounds, and organic nitrate esters, including: *n*-propylnitrate, *iso*-propylnitrate, 9-nitroanthracene, inorganic nitrite, RDX, NG, TETRYL, and isosorbide dinitrate (ISDN). In the hv-EC single electrode work, an oxidative working potential of +1.0V was used, while in the dual electrode hv-EC studies, working potentials of +1.0V and +0.8V were utilized. These dual electrode calibration plots at two different working potentials then provided us with the detector response ratios indicated above, Table 3. Figure 4 indicates the calibration plot obtained for inorganic nitrite, with a correlation coefficient of 0.9993 and a minimum detection limit (MDL) of about 0.8ng/20ul injection (40ppb). Figure 5 is a similar calibration plot for the explosive or coronary vasodilator nitroglycerin (NG), again with a coefficient of linearity in excess of 0.999. Calibration plots for RDX, TETRYL, and TNT are indicated separately in Figure 6, together with each correlation coefficient and MDL. These other minimum detection limits indicated in these calibration plots have now been improved further in the HPLC-hv-EC results described below. Figure 7 illustrates the calibration plots for two simple aliphatic nitrate esters, *n*-propylnitrate and *iso*-propylnitrate, with the amounts injected as indicated and observed EC peak heights, at a working potential of +1.0V. Figure 8 is a similar plot of linearity for the coronary vasodilator isosorbide dinitrate, with a correlation coefficient of 0.9998 and a MDL of about 12.5ng/20ul injection. One last calibration plot using single electrode hv-EC methods is presented in Figure 9, for an aromatic nitro derivative, 9-nitroanthracene, with a correlation coefficient of 0.9996 and a MDL of about 1.6ng/20ul injection. In all of these calibration plots, we have emphasized amounts injected ranging from the low ng/injection to several hundred ng/injection, or approximately two orders of magnitude in amounts studied. However, it should be emphasized here that the actual calibration plot linearities could/would exceed the upper amounts injected, but that we have been most interested in amounts involved in trace explosives work/analyses.

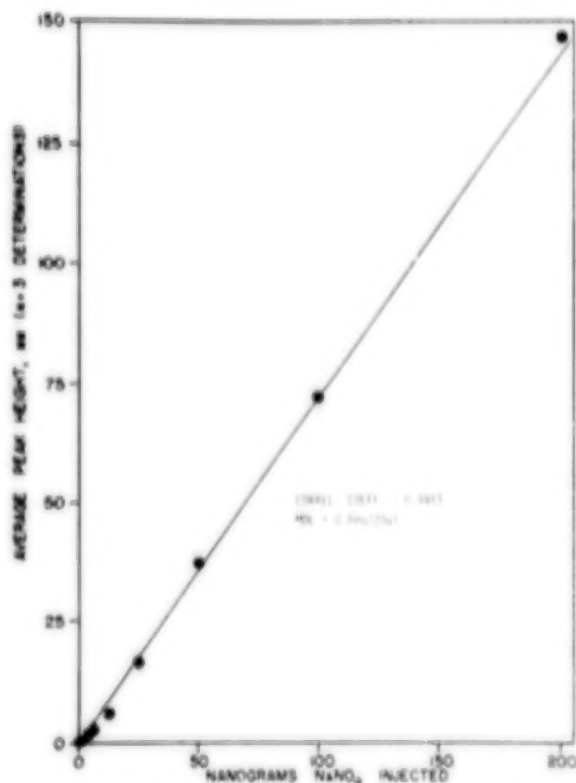


Figure 4. Calibration plot of sodium nitrite ( $\text{NaNO}_2$ ) in flow injection analysis with hv-EC using glassy carbon electrode in EC at +1.0V.

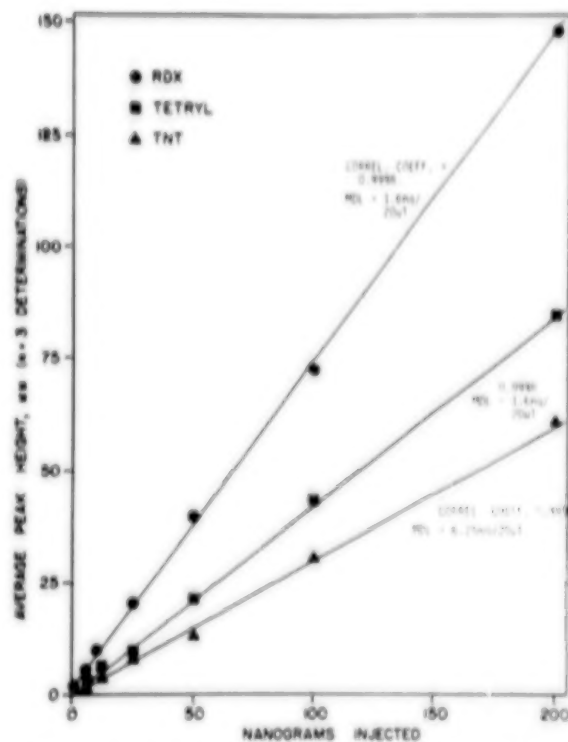


Figure 6. Calibration plots for RDX, TETRYL, and TNT using flow injection analysis with hv-EC using glassy carbon working electrode at +1.0V.

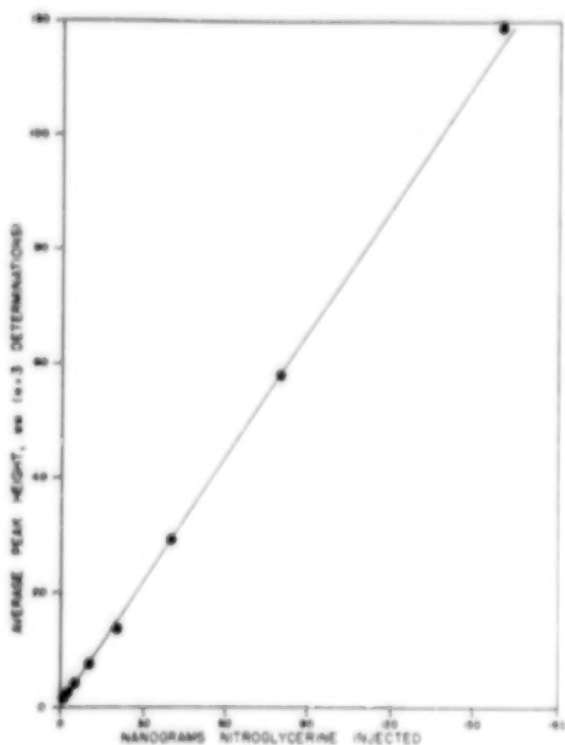


Figure 5. Calibration plot for nitroglycerin using flow injection analysis with photolysis-electrochemical detection via single electrode at +1.0V.

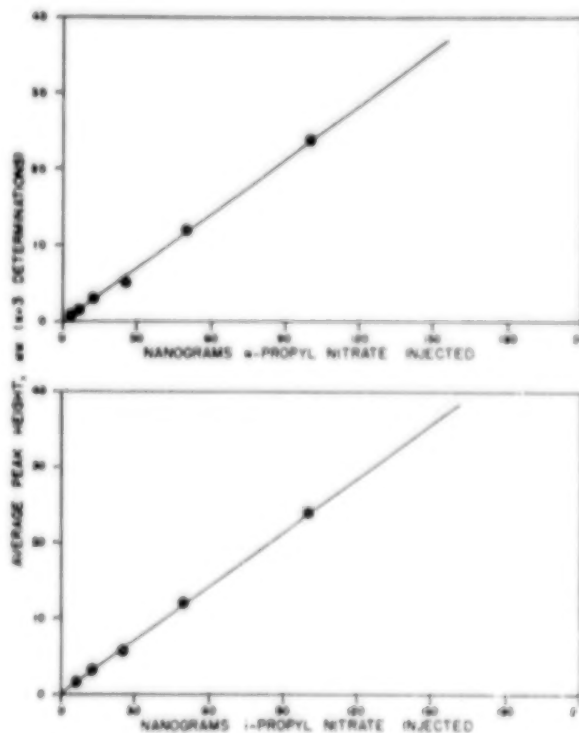


Figure 7. Calibration plots for two aliphatic nitrate esters, *n*-propylnitrate and *iso*-propylnitrate, using flow injection analysis with photolysis-electrochemical detection via single electrode at +1.0V.

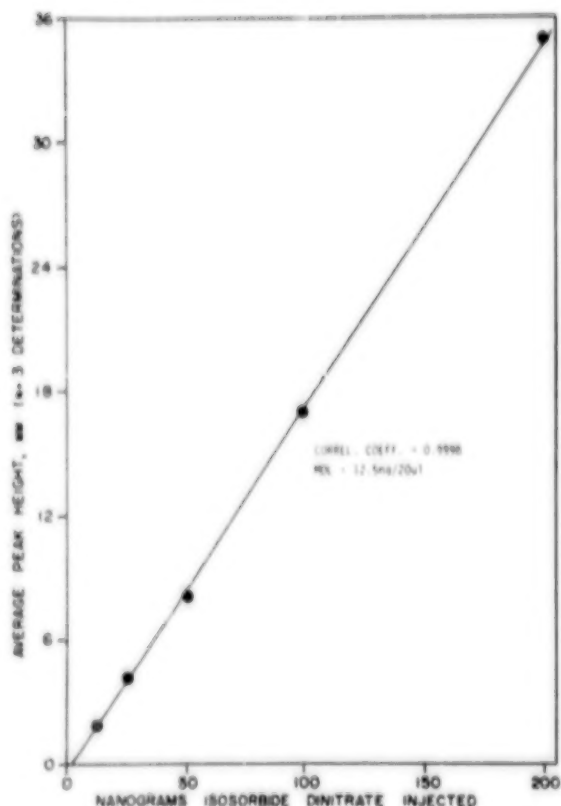


Figure 8. Calibration plot of isosorbide dinitrate in flow injection analysis with hv-EC using glassy carbon electrode at +1.0V.

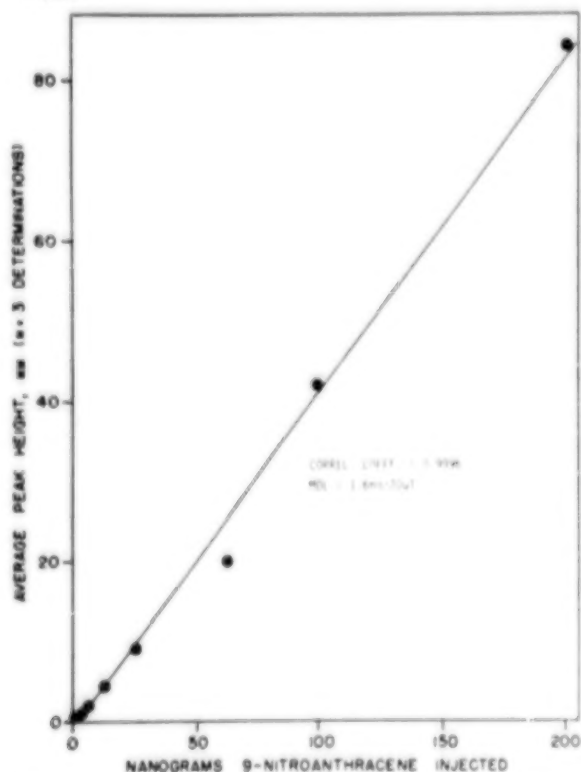


Figure 9. Calibration plot of 9-nitroanthracene in flow injection analysis with hv-EC using glassy carbon electrode at +1.0V.

A number of similar calibration plots using dual electrode detection in hv-EC are also presented here, in order to emphasize the magnitude of the differences possible in the ratios of dual detector responses for quite related analytes/compounds. Thus, Figure 10 illustrates a typical set of dual detector responses, at the working potentials indicated, for isosorbide dinitrate. This type of dual detector study then provided the response ratios already indicated above, Table 3. Figures 11-14 are the related dual detector calibration plots now obtained for four separate explosive compounds, *viz.*, RDX (Figure 11), nitroglycerin (Figure 12), TNT (Figure 13), and TETRYL (Figure 14). In all of these studies, the dual detector electrodes were operated at +1.0V and +0.8V in the parallel mode of operation, with concentrations of each compound injected ranging from the low ppm to about 10 ppm levels. However, again it must be emphasized that linearities of dual detector responses for these and other nitro derivatives should exceed the upper ranges indicated here, but that we have not yet demonstrated this experimentally. In any event, such dual detector re-

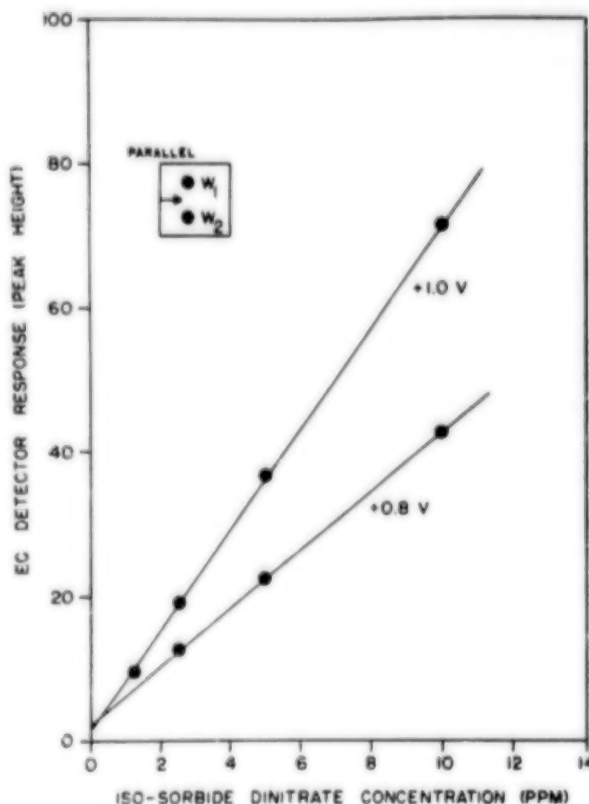


Figure 10. Plot of dual electrode EC responses, peak heights vs. concentrations of isosorbide dinitrate injected (ppm), at two different oxidative potentials, using flow injection analysis with hv-EC with EC cell in parallel orientation. Glassy carbon electrode used in EC cell.



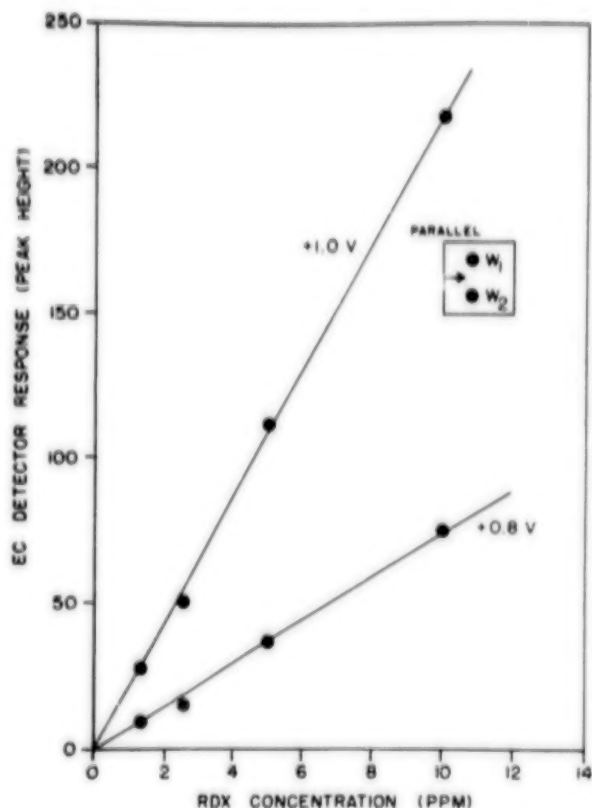


Figure 11. Plot of dual electrode EC responses, peak heights vs concentrations of RDX injected (ppm), at two different oxidative potentials, using flow injection analysis with hv-EC with EC cell in parallel orientation.

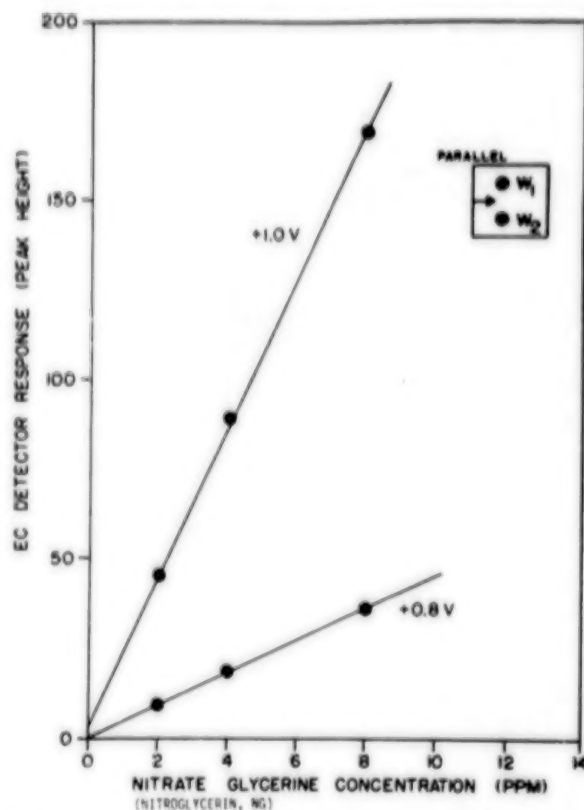


Figure 12. Plot of dual electrode EC responses, peak heights vs concentrations of nitroglycerin injected (ppm), at two different oxidative potentials, using flow injection analysis with hv-EC with EC cell in parallel set-up.

sponses are linear over at least 1-2 orders of magnitude, ranging from less than 100 ppb to at least 10 ppm.

With regard to minimum detection limits (MDL) for the explosives of interest here, these are summarized in Table 4, with the experimental conditions as indicated therein. These determinations of MDLs were made using injection volumes of 20ul, but wherein larger injection volumes have been now used, i.e., 100-200ul, such final MDLs have been reduced by a factor of 5-10 fold. Thus, for explosives such as RDX, TETRYL, and TNT, we have realized overall MDLs *via* HPLC-hv-EC methods of about 5ppb, which would appear ideal for trace analyses. It is also possible that overall MDLs could be further improved by reducing the total dead volume now present in the instrumental system, so that peak shapes and peak heights (used for MDL studies) would be further improved/optimized. All of the minimum detection limits reported here were determined using peak height measurements with a final signal/noise ratio of at least 3/1 overall.

Table 4. MINIMUM DETECTION LIMITS FOR EXPLOSIVES AND DRUGS VIA HPLC-hv-EC<sup>a</sup>

Compound Name	Minimum Detection Limit (MDL) <sup>b</sup>
RDX	500 pg = 25 ppb
TETRYL	500 pg = 25 ppb
TNT	500 pg = 25 ppb
NG	4.0 ng = 200 ppb (0.200 ppm)
ISDN	2.5 ng = 125 ppb (0.125 ppm)
NaNO <sub>2</sub>	1.56 ng = 78 ppb

- HPLC-hv-EC conditions used a C-18 RP column, 3um, 10-cm x 4.6-mm i.d., with mobile phase of 50/50 MeOH/0.1M NaCl, 0.6 ml/min flow rate, +0.8V oxidative EC detection.
- Injections were made in 20ul volumes, MDL given in terms of mass of analyte injected and concentration, ppb = parts-per-billion; ppm = parts-per-million, etc.

#### Single Electrode EC Detection *via* HPLC-hv-EC for Explosives and Drugs

We have now utilized both single and dual electrode detection for various explosives mixtures, but because the dual approach provides more qualitative and quantitative information on a single injection, these have been emphasized

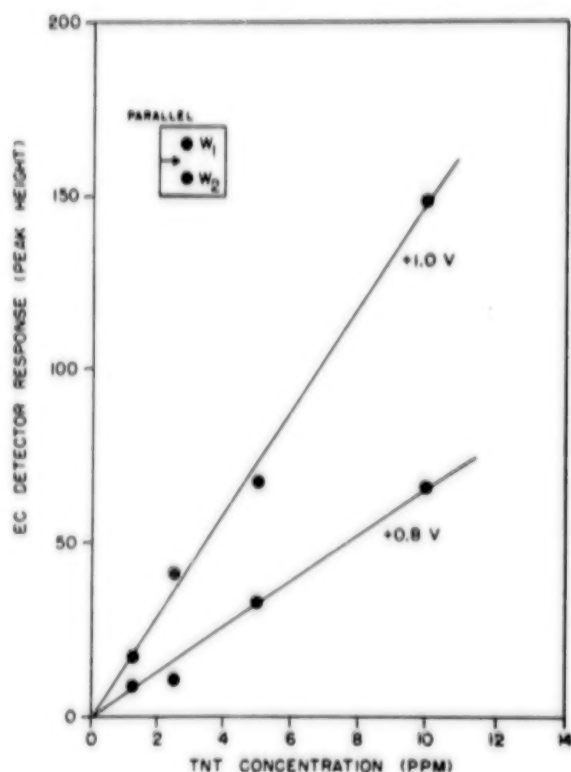


Figure 13. Plot of dual electrode EC responses, peak heights vs concentrations of TNT injected (ppm), at two different oxidative potentials, using flow injection analysis with hv-EC with EC cell in parallel orientation.

throughout. Figure 15 illustrates a typical single electrode chromatogram (A) for three standard explosives, *viz.*, RDX, TETRYL, and TNT, with the irradiation lamp turned on and the detector at +1.0V working potential. Figure 15B is the same HPLC-hv-EC analysis of these same three explosives, but now with just the lamp turned off, all other operating parameters identical to those in Figure 15A. Finally, Figure 15C indicates the single electrode response for a mixture of NG and ISDN, with specific analytical parameters as indicated. Mannitol is present in Figure 15C because it was present in the sample of ISDN utilized in these studies, but since it is chromatographically resolved from the ISDN and NG, it does not present any analytical problems. Clearly, as Figures 15A and 15B so clearly demonstrate, detection of these and other explosives/drugs/nitro compounds, is entirely dependent on the irradiation step, on-line, post-column, for the generation of the EC detectible species (nitrite, etc.). Although the +1.0V working potential used here was optimal for these particular analytes, it is clear that a vari-

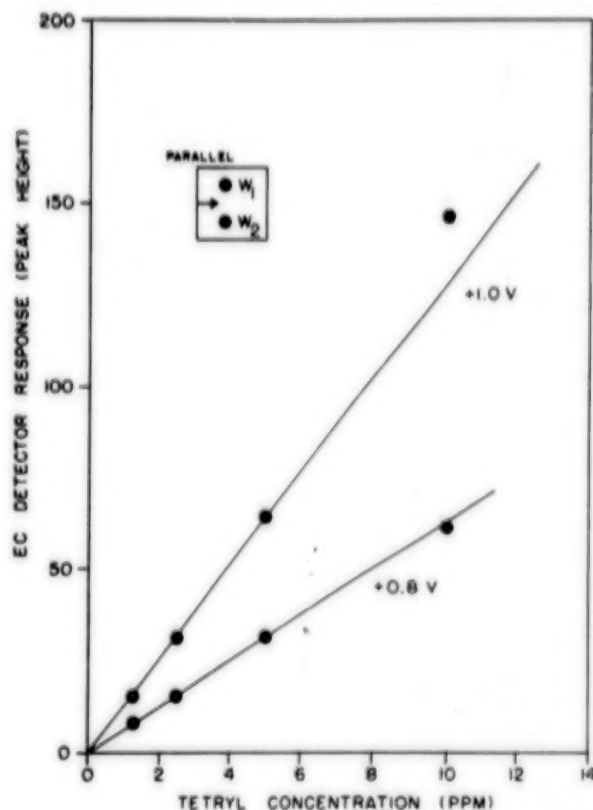


Figure 14. Plot of dual electrode EC responses, peak heights vs concentrations of TETRYL injected (ppm), at two different oxidative potentials, using flow injection analysis with hv-EC with EC cell in parallel orientation.

ety of other oxidative and perhaps reductive working potentials could also be used in this HPLC-hv-EC work. That is, inorganic nitrite, as an irradiation product of various explosives, can be detected oxidatively, but others have already shown that underivatized explosives can also be detected in the reductive EC mode of operation [Bratin *et al.* (1981)]. Hence, it should be possible to utilize both oxidative and reductive dual electrode detection for these explosives, with and without the irradiation lamp turned on in HPLC-hv-EC approaches. Thus, with the lamp off, only reductive EC detection would/should be possible, but with the irradiator on, oxidative EC should detect nitrite and reductive EC would detect intact explosives or nitro compounds. Thus, although single electrode detection is useful and practical for real world samples, dual electrode detection in LCEC or HPLC-hv-EC or hv-EC can provide significant qualitative and quantitative advantages, as indicated/summarized below.

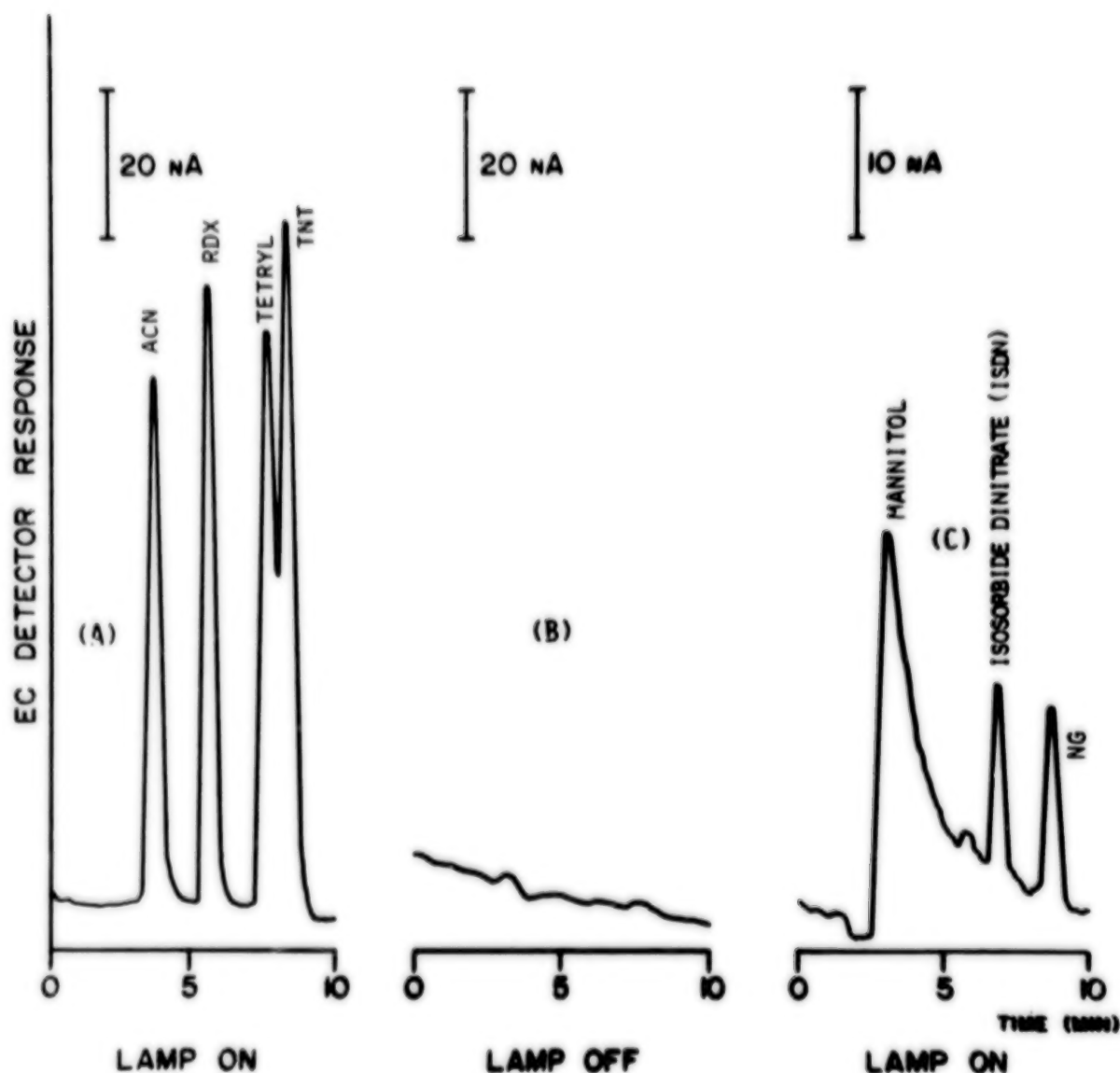


Figure 15. HPLC-hv-EC single electrode chromatograms for three explosives: RDX, TNT, and TETRYL standards, using RP C-8 reversed phase column, 10um, 25-cm x 4.6-mm i.d., with 50/50 MeOH/0.1M NaCl mobile phase at 1.4 ml/min, glassy carbon electrode operated at +1.0V oxidatively. (A) hv lamp turned on; (B) hv lamp turned off; (C) hv lamp on with NG and ISDN standards injected.

#### Dual Electrode Detection in HPLC-hv-EC for Explosives and Drugs

Figure 16 illustrates a typical dual electrode, oxidative/oxidative parallel HPLC-hv-EC set of chromatograms for a mixture of three standard explosives, RDX, TETRYL, and TNT, with conditions as indicated. Detection here used EC methods in the parallel mode, with a glassy carbon working electrode operated at +1.0V and +0.8V. Once again, alternative oxidative/oxidative, oxidative/reductive, and/or reductive/reductive potentials are possible and practical here, as above

with the single working electrode situation. The next set of dual electrode HPLC-hv-EC chromatograms, Figure 17, is almost identical in operating conditions and amounts of explosives injected to those used to derive Figure 16 chromatograms. The only difference is that one of the two dual electrodes in Figure 17 is operated at +0.90V, rather than the +0.80V used for this second electrode in Figure 16. The other working electrode in both Figures 16 and 17 has been maintained at +1.0V throughout. The responses thus observed at the +1.0V electrode in both Figures are about



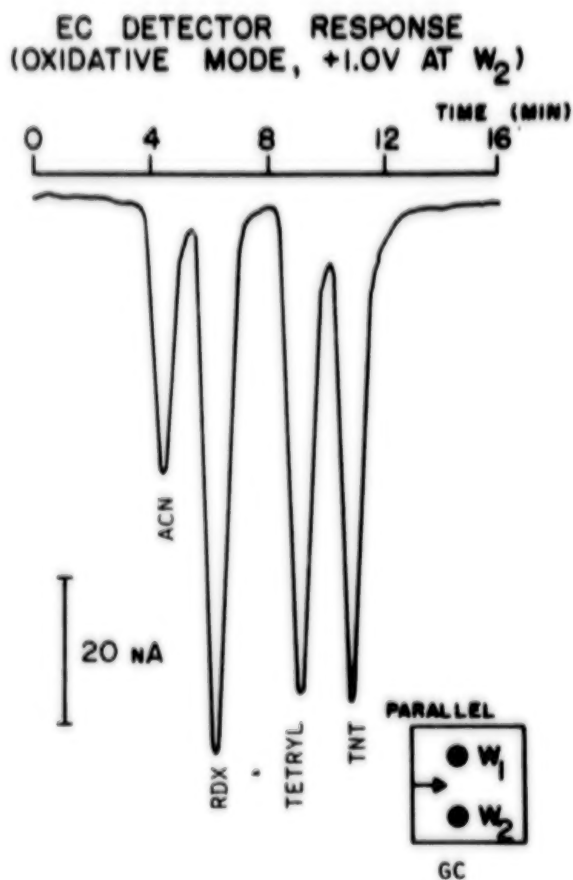


Figure 16. HPLC-hv-EC dual electrode chromatograms of three explosives, TDN, TETRYL, and TNT, using C-18 RP, 3 $\mu$ m, 10-cm x 4.6-mm i.d. column with 50:50 MeOH/0.1M NaCl at 0.6 ml/min flow rate. Dual electrodes operated in oxidative/oxidative modes.

the same in peak heights, but the responses at the +0.90V electrode in Figure 17 are much greater/larger than those at the +0.80V electrode in Figure 16, as expected from the linear hydrody-

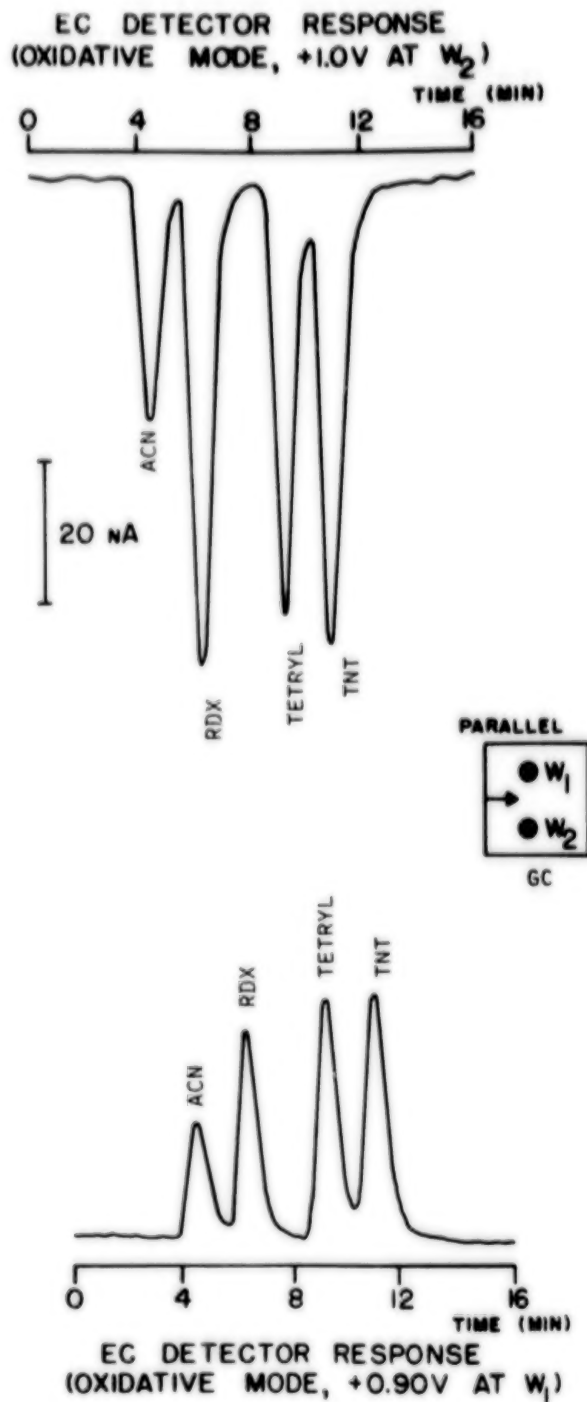


Figure 17. HPLC-hv-EC dual electrode chromatograms of three explosives, RDX, TETRYL, and TNT, using C-18 RP, 3 $\mu$ m, 10-cm x 4.6-mm i.d. column with 50:50 MeOH/0.1M NaCl at 0.6 ml/min flow rate. Dual electrodes operated in oxidative/oxidative modes, glassy carbon surfaces.

namic voltammogram obtained initially for nitrite ion.

Figure 18 illustrates another set of dual electrode HPLC-hv-EC chromatograms, herein util-

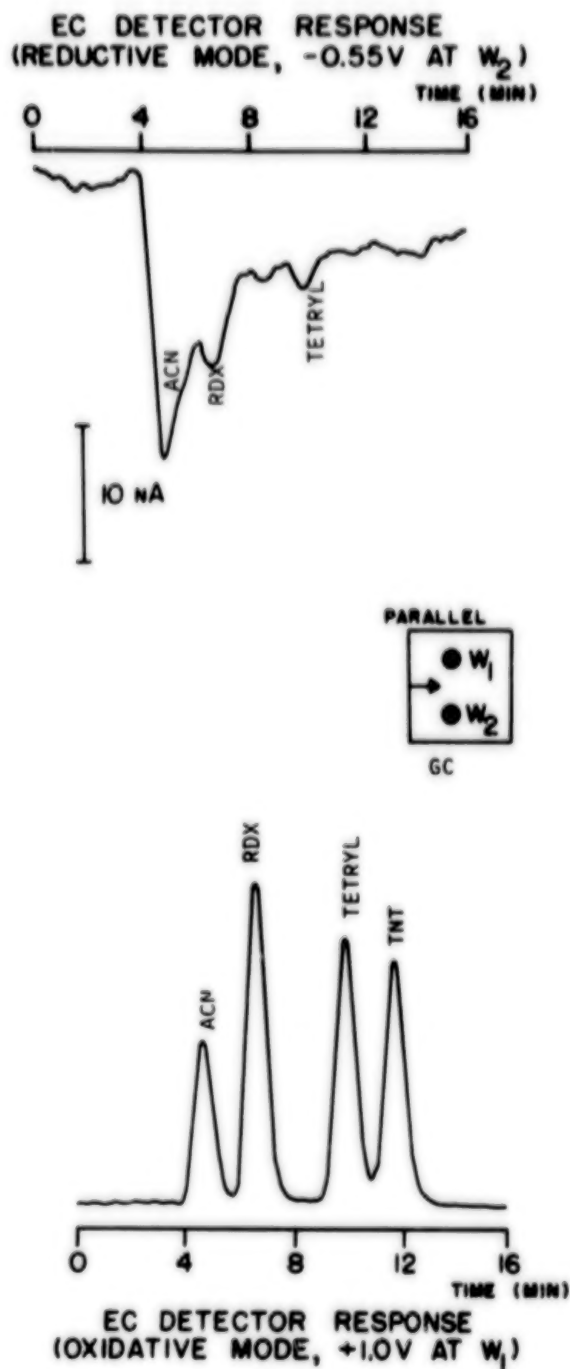


Figure 18. HPLC-hv-EC dual electrode chromatograms for the three explosives, RDX, TETRYL, and TNT, using C-18, RP column, 3 $\mu$ m, 10cm x 4.6-mm i.d., 50/50 MeOH/0.1M NaCl mobile phase at 0.6 ml/min flow rates. Glassy carbon dual electrodes operated in oxidative/reductive modes.

izing oxidative/reductive approaches, with one working electrode held at -0.55V and the other at +1.00V, for the three explosives of interest, RDX, TETRYL, and TNT. Although the reductive responses for these three explosives, at the lev-

els injected here, are somewhat poor, at least RDX and TETRYL are discernible above the background noise level. We believe that the responses observed here and elsewhere for these nitro compounds at the reductive potential of -0.55V are arising from electrochemical reduction of the starting, intact analyte, underivatized, with the nitro groups still intact despite having gone through the irradiator with the lamp on. If all of these explosives had been fully irradiated to form nitrite ions, and none of the original compounds remained, then there would not be any response at the reductive working electrode. Wherein these same studies are performed with the lamp turned off, only the reductive chromatogram in Figure 18 remains, at somewhat greater peak heights for each explosive, since now none is being destroyed/photolyzed with the lamp off. Similarly, Figure 19 illustrates the same type of dual detector responses in HPLC-hv-EC, oxidative/reductive, for the two drugs ISDN and NG, with the specific operating conditions as indicated. The other peak in Figure 19 is due to mannitol, which happens to be present in the particular sample of ISDN utilized/available for these studies. Again, in both oxidative and reductive EC operating modes, each of these two nitrate esters, NG and ISDN, provide significant responses under HPLC-hv-EC conditions. We believe that in this situation, the oxidative response is due to nitrite released from the nitrate esters, and the reductive response is due to nitrate ( $\text{NO}_3^-$ ) released from the same nitrate ester precursors. With the lamp turned off here, there are no EC responses in either the oxidative or reductive modes. The dual electrode EC analysis for ISDN and NG has also been performed in HPLC-hv-EC with both working electrodes in the oxidative modes, Figure 20. Here, one of the two glassy carbon working electrodes is operated at +1.0V and the other at +0.9V, with the other operating conditions as indicated. The dual detector response ratios for these two compounds in Figure 20 are clearly quite different from the similar ratios that would be obtained from these same compounds in Figure 19. Thus, dual detector response ratios can be easily obtained *via* two separate injections of the same analytes with appropriate changes in the operating potentials of the two working electrodes.

#### Dual Electrode HPLC-hv-EC Detection of Real World Explosion Debris Samples

Figure 21 is a set of HPLC-hv-EC dual electrode chromatograms for a real world sample re-

EC DETECTOR RESPONSE  
(REDUCTIVE MODE,  $-0.55\text{V}$  AT  $W_2$ )

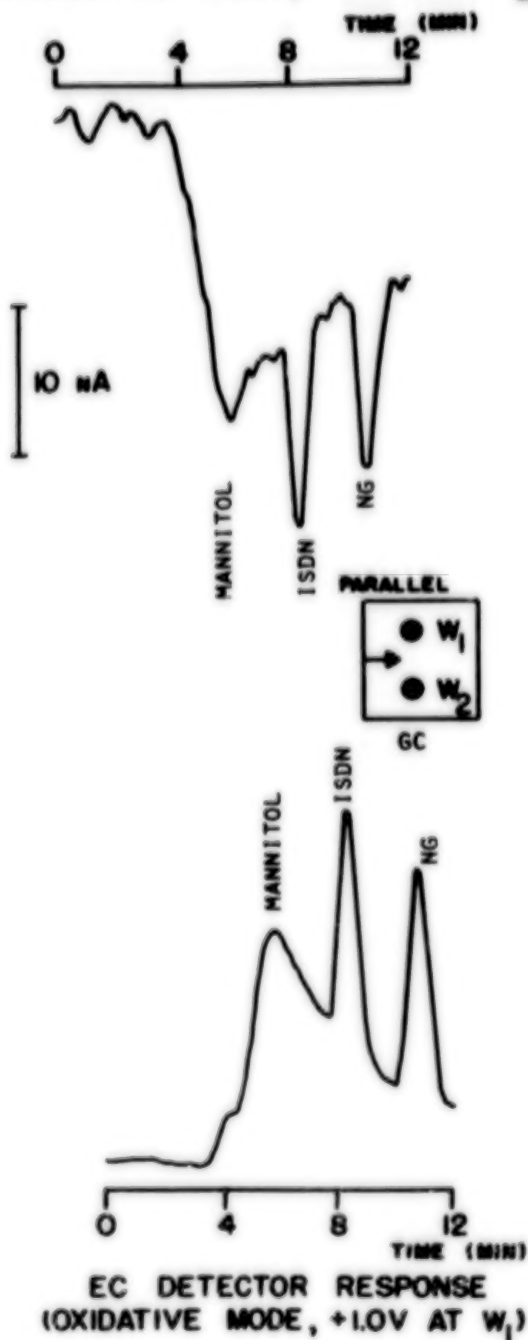


Figure 19. HPLC-hv-EC dual electrode chromatograms for the drugs NG and ISDN, using C-18 RP,  $3\mu\text{m}$ , column,  $10\text{-cm} \times 4.6\text{-mm}$  i.d., 50/50 MeOH/0.1M NaCl mobile phase at 0.6 ml/min flow rate. Dual electrodes operated in the oxidative/reductive modes, glassy carbon surfaces.

sulting from a pipe bomb blast under a private car, wherein the post-blast debris was first extracted with acetonitrile. This solution was then pre-concentrated, and analyzed first by thin-layer

EC DETECTOR RESPONSE  
(OXIDATIVE MODE,  $+1.0\text{V}$  AT  $W_2$ )

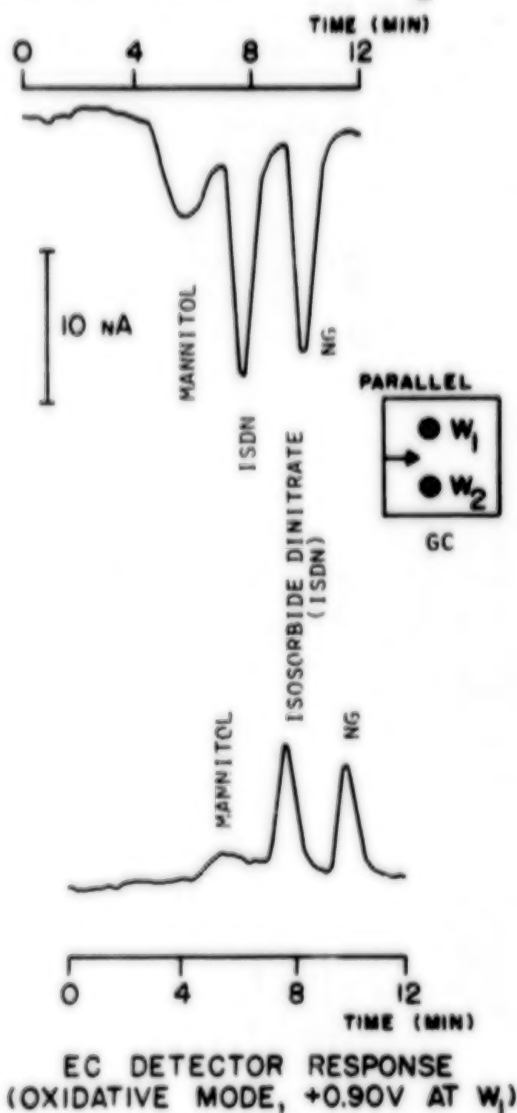


Figure 20. HPLC-hv-EC dual electrode chromatograms for the drugs NG and ISDN using C-18, RP,  $3\mu\text{m}$  column,  $10\text{-cm} \times 4.6\text{-mm}$  i.d., 50/50 MeOH/0.1M NaCl mobile phase at 0.6 ml/min flow rate. Dual glassy carbon electrodes operated in oxidative/oxidative modes, as indicated.

chromatography (TLC) within the labs of the Bureau of Alcohol, Tobacco, and Firearms (U.S. Treasury Department). This TLC analysis indicated the possible presence of NG, and this was then verified and confirmed using our HPLC-hv-EC approaches. Although this particular sample contained crankcase oil together with the NG, the NG was satisfactorily resolved and separated from such other interferences present by the HPLC conditions used. The NG could then be

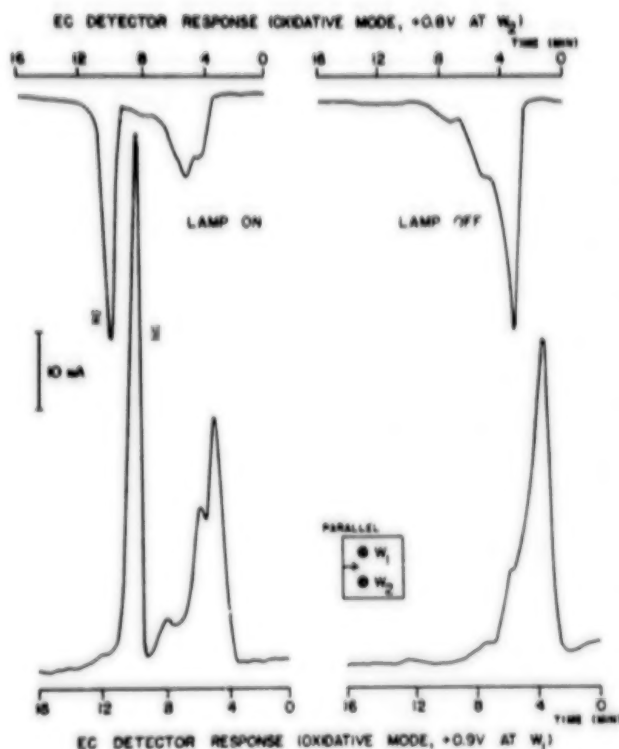


Figure 21. HPLC-hv-EC dual electrode chromatograms for a real world sample of post-blast debris extracts containing NG by TLC analysis. Conditions used a RP, C-18 column, 3 $\mu$ m, 10-cm x 4.6-mm i.d., 50/50 MeOH/0.1M NaCl mobile phase at 0.6 ml/min flow rate, glassy carbon dual electrodes operated in oxidative/oxidative modes, as indicated.

clearly identified and determined with the irradiation lamp turned on, Figure 21 (left). Indeed, the two chromatograms in Figure 21 were obtained first with the lamp on (left) and then with the lamp off (right). With the lamp off, only the interferences were observed, but no peak is seen at the known/determined retention time ( $t_r$ ) for a standard of NG. With the lamp turned on, Figure 21 (left), NG is now clearly evident, at the correct retention time/volume for the standard NG. Thus, these results, using dual electrode detection, at the working oxidative potentials of +0.8V and +0.9V, together with the lamp on/off method, strongly confirm the original TLC identification of NG being present in this particular real world sample of debris extracts. This information is in addition to the more customary identification in HPLC based on retention times/volumes vs a standard injected under identical analytical conditions. Were additional confirmatory evidence necessary, this could readily be obtained by comparing the dual electrode response ratios at various working potentials for the suspected NG in this

sample with the same ratios obtained for authentic NG analyzed under the same set of HPLC-hv-EC conditions. Indeed, when this was determined for this sample, these two set of detector response ratios were identical within experimental error/conditions. Thus, these overall methods of trace explosives analysis provide a very high, perhaps unique, degree of analyte specificity for individual explosives present in complex real world samples.

## CONCLUSIONS

We have now developed, optimized, and applied a somewhat newer approach for the trace analysis of organic nitro compounds and explosives/drugs. These overall HPLC-hv-EC methods have been applied to a number of standard explosives and organic nitro compounds, using both single and dual electrode detection. Such overall methods have also been applied to certain real-world, post-blast explosion debris extracts suspected of containing NG. We have demonstrated the dual electrode responses for various explosives and related nitro compounds, as a function of the working potentials applied, by plotting amounts injected in terms of concentrations (ppm) or absolute amounts (ng) vs peak heights/currents generated. The overall selectivity of these methods far exceeds that already possible *via* single electrode HPLC-hv-EC methods. It has further been shown that these overall approaches for the determination of nitro compounds can be readily and quickly applied to materials such as: explosives, drugs and veterinary products, nitrate ester compounds, nitro aromatics, nitro-PAHs, and related nitro derivatives, be these O-nitro, C-nitro, or N-nitro in nature. Calibration plots and linearities of EC response in both single and dual electrode methods for various nitro compounds have also been determined and described, together with certain established minimum detection limits using these HPLC-hv-EC methods of analysis. It is suggested by these results that hv-EC (FIA) and HPLC-hv-EC analytical approaches should find wide applicability and acceptance in a number of areas of trace organic or inorganic analysis. Such extensions of the work already completed and described here are already in progress in our laboratories.

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Abbreviations used:

HPLC = high performance liquid chromatography; hv = photolysis/photohydrolysis/photochemical derivation; EC = electrochemical detection; UV = ultraviolet detection; HOH = water; MeOH = methanol; MDL = minimum detection limits; ppm = parts-per-million; ppb = parts-per-billion; NO<sub>2</sub><sup>-</sup> = nitrite ion; N-NO = N-nitroso compound; ml/min = milliliters per minute; V = volts; nA = nanoamperes; GC = gas chromatography; TEA = Thermal Energy Analysis; MS = mass spectrometry; ECD = electron capture detector; LCEC = liquid chromatography-electrochemistry; TNT = 2,4,6-trinitrotoluene; DNT = dinitrotoluene; NG = nitroglycerin; RDX = 1,3,5-tri-

tro-1,3,5-triazacyclohexane; TETRYL = 2,4,6,N-tetranitro-N-methylaniline; NO<sub>3</sub><sup>-</sup> = nitrate ion; FIA = flow injection analysis; hv-EC = photolysis-electrochemical detection.

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# SCREENING FOR ORGANIC EXPLOSIVES COMPONENTS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH DETECTION AT A PENDENT MERCURY DROP ELECTRODE.

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**ABSTRACT.** The electrochemical detection of explosives components, separated by high performance liquid chromatography (HPLC), at a mercury film (thin layer) electrode (MFE) can be improved considerably both in ease of use and sensitivity at a pendent mercury drop electrode (PMDE). The electrode characteristics are highly reproducible, the electrode may be renewed during or at the start of a chromatogram, and it is not subject to the contamination problems of the MFE. With 3  $\mu\text{m}$ -particle HPLC columns the detection limits for a wide range of nitrate and nitro compounds are at present 2–20 pg per 10  $\mu\text{l}$  injected sample. These limits are approximately a tenfold improvement on those reported for the MFE technique, and are comparable with those of electron capture detection in gas chromatography, compared with which technique the PMDE is superior in specificity. A facile clean-up procedure has been developed to enable the PMDE-HPLC technique to be used for screening handswabs for traces of the explosives components. Examples of the application of the technique are presented. (British Crown copyright reserved.)

## Mercury-Film Electrodes

I wish to present some work arising from the important contribution that has been made to the chromatographic characterization of explosives by Dr Kissinger and his colleagues.<sup>1</sup> As Dr Kissinger has described, organic explosives components can be detected by the reduction current they generate at glassy carbon or mercury film on amalgamated gold electrodes. With fairly clean samples I have obtained results entirely in agreement with Dr Kissinger's, and with excellent detection limits. However I ran into problems due to electrode contamination effects when samples from soiled handswabs were analyzed.

Figure 1 shows an example from the high-performance liquid chromatography (HPLC) of a handswab, detected at a mercury film electrode (MFE). The passage of the sample through the detector has resulted in a disrupted base line. The effect of further samples is additive, so that a succession of them rapidly makes the system unusable. Of course, the electrode can be stripped down and cleaned, which was done daily in any case, or the presumably deposited material can be dis-

charged if the electrode potential is briefly set to zero. But either way a considerable loss in running time occurs.

## Mercury Drop Electrodes

An obvious remedy here is to use a dropping mercury electrode—a polarographic detector—in which a new electrode can be formed as rapidly as several times a second. But with this electrode I found—as, indeed, have many others—that the sensitivity is severely restricted by the noise level generated in the formation and dislodgement of the mercury drops.

A great improvement is to use a hanging mercury drop electrode, and to renew the electrode only when necessary. And an even further improvement can be made with a so called "pendent" mercury drop electrode<sup>2</sup>, although "squashed" would be a more accurate description. This is illustrated in Figure 2. It is a slightly modified version of a cell sold by Princeton Research. The original is intended to hang an unsupported drop from the Hg capillary in the eluent stream, which impinges on the drop from below

MFE -1.0 V

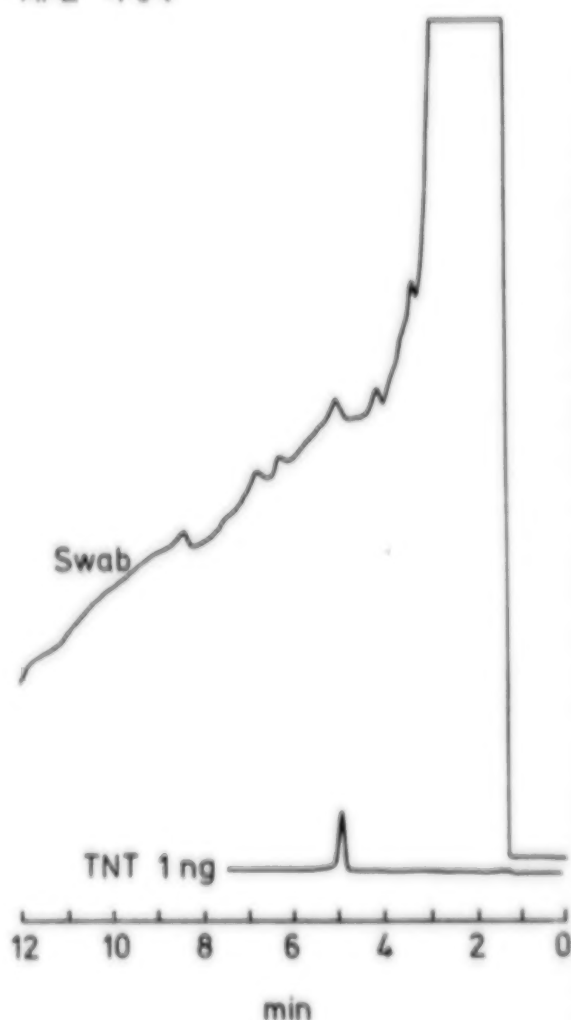


Figure 1. Chromatogram of a handswab extract detected at a mercury film electrode maintained at  $-1.0$  V vs. Ag/Ag Cl, and a chromatogram of 1 ng TNT under the same conditions. The chromatographic conditions are given in Table I.

In the modified cell, the distance between the capillary tip and the eluent jet is continuously variable, and the jet orifice is opened-up to 0.8 mm. Hence, an increased drop-size relative to the tip-to-jet separation may be used; or a small drop can be introduced directly into the widened orifice. The effect of the modification is to give some increase in absolute sensitivity in terms of signal-to-noise ratios; but, most importantly, such drops can be left in position without any possibility of their falling from the capillary tip—in contrast to the hanging drop electrode. For a given tip-to-jet separation the optimum drop is slightly distorted due to mechanical compression and to the impinging eluate.

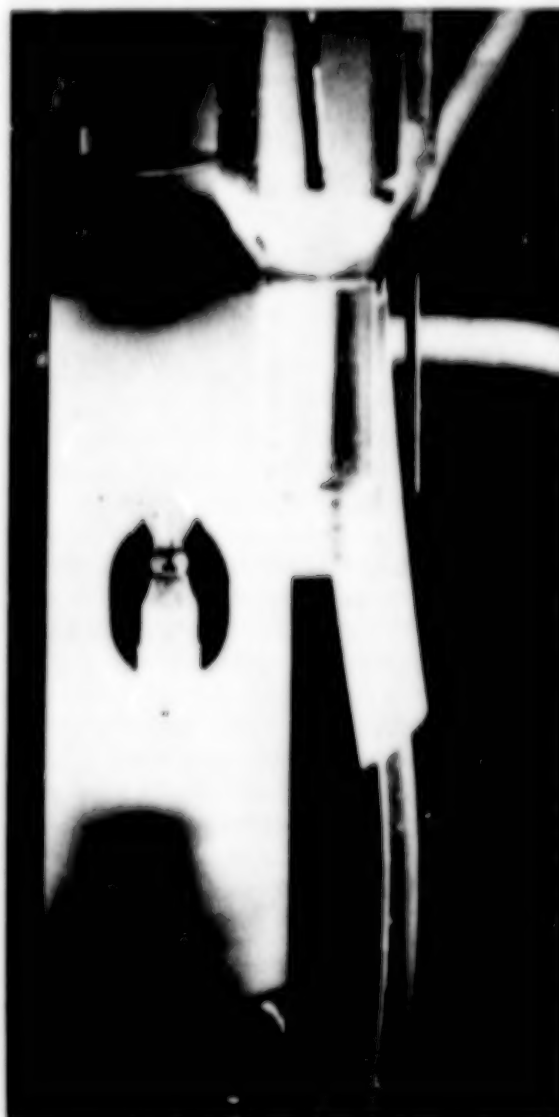


Figure 2. The pendent mercury drop electrode (PMDE). The drop is located between the two opposed nozzles seen through the assembly's porthole. The long dimension of the photograph represents 4 cm at the cell position.

#### HPLC Conditions

For HPLC the detector is used in conjunction with a 3-micron column with an aqueous methanol eluent buffered to pH 3.0 with phosphate (Table I). I find the most efficient way to do the essential deoxygenation of the eluent reservoir is to keep the eluent under reflux continuously. This gives much lower levels of oxygen than a prolonged nitrogen purge, although I do use a nitrogen bleed to provide nucleation for the boiling solvent. I do not now include a chelating agent in my solvent, because this seems to increase the base

line signal, presumably because traces of heavy metals are eluted from the chromatographic equipment.

**Table 1. HPLC CONDITIONS**

Column packing	ODS-Hypersil, 3-micron.
Column dimensions	Length, 15 cm; i.d., 4.5 mm.
Solvent	Methanol + aqueous phosphate (0.025 M, pH 3.0), 100 + 86 by volume.
Temperature	Ambient (>22 °C)
Flow	1 ml min <sup>-1</sup>
Detection	Pendent mercury drop (26 mg at a tip-to-jet separation of 0.9 mm; or 3.2 mg at a separation of 0.4 mm) in a modified PARC 310 polarographic detector. The electrode potential was usually -1.0 V vs Ag/AgCl.

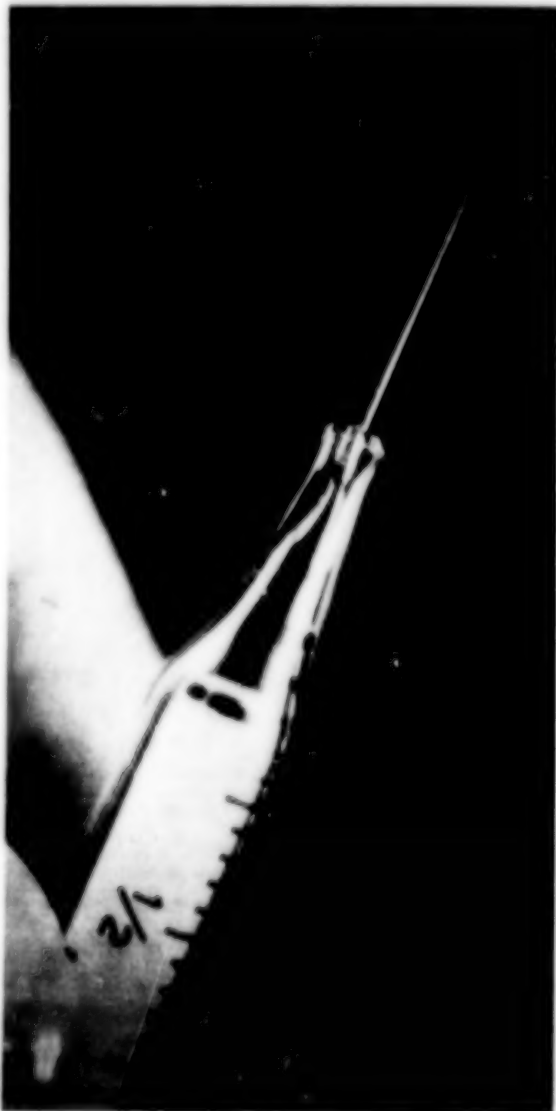


Figure 3. Modified 1 ml syringe for sample deoxygenation and injection.

### Sample Deoxygenation

Apart from the eluent, samples too must be deoxygenated. There is a very simple way of doing this with small samples<sup>3</sup>. All that is needed is a modified glass hypodermic syringe. This is shown in Figure 3. The end of the syringe has been pulled down, and a Rheodyne-size needle expoxied into it. As Figure 4 shows, the injector is set upright with a nitrogen purge attached to the solvent waste line from the inject position of the injector, so that all that is necessary is to withdraw a portion of the sample into the syringe, set the syringe into the injector, pass nitrogen through it for 2 minutes and then make the injection in the usual way.

### Chromatograms—Standard Compounds

This (Figure 5) is a chromatogram of a standard mixture of compounds. Each peak represents 0.5ng of the 18 compounds, which are separated within eight minutes. All of the actual compounds are listed in Table 2 according to their numbering on the chromatogram. As the chromatogram shows, the drop is changed immediately before the start of the chromatogram.

There are one or two points that must be made here concerning the use of 3-micron-particle col-

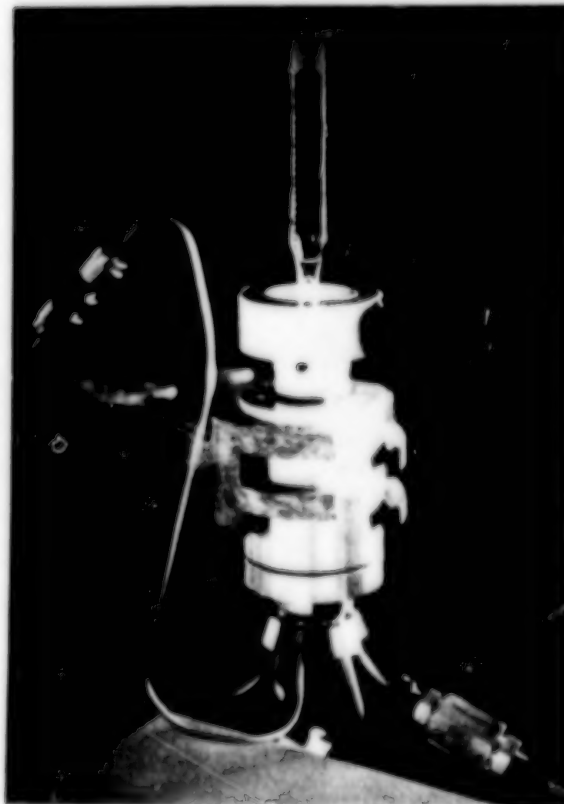


Figure 4. Sample, in modified syringe, during deoxygenation.

umns. The sensitivity obtained from them, compared with 5-micron columns, is practically doubled provided efficient columns of the same theoretical plate count are compared. This follows, of course, from the reduction in peak widths because the columns are shorter. But it cannot be too strongly emphasized that the solvent in which the sample is dissolved must closely match the eluent in composition. If it doesn't, a catastrophic loss in resolution occurs. Provided care is taken over this, surprisingly large sample volumes can, if necessary, be injected without an unreasonable loss in resolution. This particular chromatogram (Figure 5) is from a 10- $\mu$ l injection. With 20- $\mu$ l injections excellent chromatograms are still obtainable. And even with 50- $\mu$ l some useful chromatography can still be done for the later-eluting peaks. A final point here: I find that the columns are just as easy to pack, and that they last just as well as those packed with 5-micron particles.

Table 2. STANDARD EXPLOSIVES COMPOUNDS

Numbered according to Fig. 5

- 1 Nitroguanidine
- 2 Octogen (HMX)
- 3 Styphnic acid
- 4 Picric acid
- 5 Hexogen (RDX)
- 6 Ethyleneglycol dinitrate (EGDN)
- 7 Isosorbide dinitrate
- 8 *m*-Dinitrobenzene
- 9 Tetryl
- 10 Nitrobenzene
- 11 Nitroglycerine (NG)
- 12 2,4,6-Trinitrotoluene (TNT)
- 13 2,6-Dinitrotoluene
- 14 2,4-Dinitrotoluene
- 15 *o*-Nitrotoluene
- 17 *m*-Nitrotoluene
- 18 Pentaerythritol tetranitrate (PETN)

#### Detection Limits

The detection limits of the technique vary, according to the compound, in the region 2–20 pg. These (Figure 6) are examples of chromatograms of amounts of explosive compounds in this range. The lowest sensitivity here is for PETN, the highest for the polynitro aromatic compounds. At the 5 pg level, RDX and EGDN are obscured by residual oxygen.

The pressure pulsation of the pump used here, about 0.5%, evidently makes no contribution to the noise level, although if the background current is allowed to rise, e.g. due to traces of oxygen, a regular pulsation (depending in detail on the drop

#### NITRO/ATE COMPOUNDS (0.5 ng)

3.2 mg PMDE

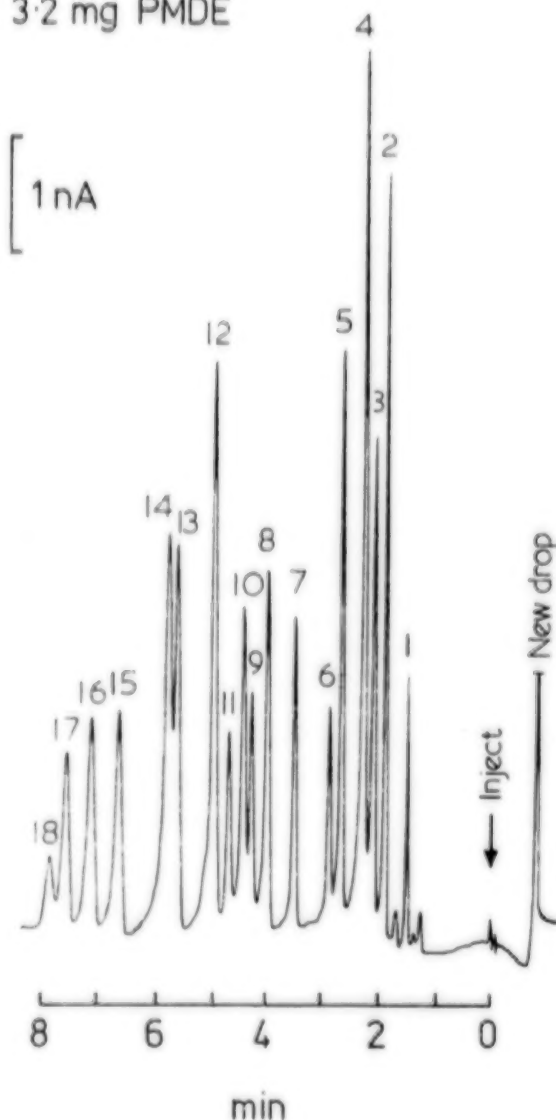


Figure 5. Chromatogram (PMDE) of standard explosives compounds. The identities of the compounds are given in Table 2.

size) becomes apparent. The background current in these chromatograms was about 4.5 nA.

These chromatograms are from 10- $\mu$ l injections, hence the results in terms of concentration sensitivity are in the same region as electron capture detection in gas chromatography. They are also much lower than the results originally reported for thin layer electrodes, but I imagine similar results would be obtained for both detectors given columns of similar efficiency. The important point here is that we now have a sensitive electrode that may be renewed the instant that this is re-

quired, and that in any case the electrode is much less sensitive to contamination effects.

Here (Figure 7) is the example from the thin film electrode experiment with hand swab material shown initially. It is compared here with a chromatogram detected at a PMDE, adjusted to give the same response with respect to TNT. Obviously the problem of the disrupted base line is largely dealt with. Clearly there is some displacement, but this does not interfere in an analysis after the initial peak, and the base line is completely restored when a new drop is formed for the next analysis.

#### Sample Clean-up<sup>4</sup>

The comparison here (Figure 7) has been made with a sample that has not been cleaned-up, and both techniques give improved results with cleaned up samples. But even with these the same problems persist particularly with the thin film electrode.

In one respect the HPLC system is more de-

manding in the type of sample it will accept than the more usual gas chromatography techniques. This arises because of the solvent-matching requirement that I have already mentioned.

One obvious response to the problem is to use the HPLC solvent for swabbing. But it doesn't work! The solvent composition changes during swabbing because of the accumulation of water from sweat and because of evaporation. Hence, any solvent on a swab must be removed. One may use dry swabs: these remove explosives from hands quite effectively. But, apart from the moisture problem, volatile explosives components are lost very rapidly from dry swabs. These components are also lost if an attempt is made to evaporate the solvent from a swab. Another problem is that fats and oils are often present in large amounts, and need to be removed to protect the column from contamination.

The solution to these problems is contained in a BAS centrifugal microfilter, as shown in Figure 8. The filter is packed with a mixture of 50 mg each of 10-micron alumina and 10-micron ODS—Spherisorb, and a piece of Viton sleeving is fitted

#### SENSITIVITY LIMITS

3.2 mg PMDE

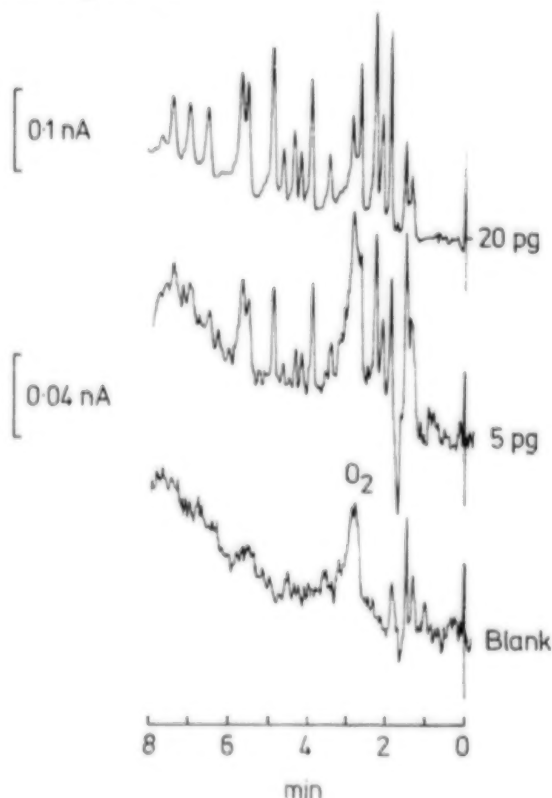


Figure 6. Chromatograms (PMDE) of standard compounds (Table II) in the region of their detection limits.

#### HANDSWAB

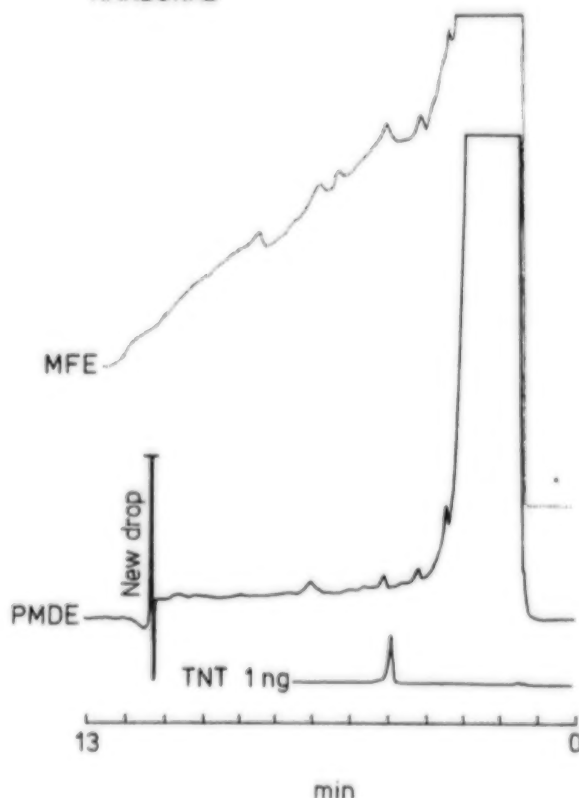


Figure 7. The same samples as in Figure 1 with a chromatogram detected at a PMDE.



to the outside of the filter holder so that the assembly can be attached to a vacuum line. These assemblies are made up in batches and stored away until required. Immediately before use ethanol is spun through the adsorbent. The swab is loosely inserted in the top of the filter, a silica gel trap is fitted to the top, and the lower end attached to the vacuum line so that a stream of dried air may be drawn through the swab and then through the adsorbent. With ethanol as a swabbing solvent the time-to-dryness is about  $\frac{1}{2}$  hour. This can be checked if necessary by weighing the assembly at 5 minute intervals around the time when evaporation is thought to be nearing completion.

If the swab is overwet, solvent may exude when the swab is pushed into the microfilter. In this case the surplus is removed, and the assembly inverted during the drying to avoid any solvent's running onto the adsorbent. The surplus can be returned to the dried swab, which is then redried, although it is likely that sufficient sample for analysis will remain on the swab in the first instance.

The swab is now packed down onto the adsorbent, and the whole eluted with aqueous methanol (35 + 100, by volume) to give *ca.* 170 microlitres of extract. If this is collected in a tared tube, the composition of the extract is readily adjusted, using its mass, to that of the eluent.

During this process the following has occurred:

1. The solvent remaining on the swab and in the adsorbent has been removed.
2. Any explosives components that have volatilized from the swab are mostly trapped out on the ODS-Spherisorb.
3. During the elution, fatty and oily materials are trapped on the ODS-Spherisorb, whilst the explosives components run through.
4. The alumina traps out much of the electroactive material that gives rise to the initial chromatography peak.

A variety of recovery experiments made with used handswabs gave recoveries in the region 80-90%, depending on the nature of the swab and on the compound concerned.<sup>4</sup>

#### Selectivity Considerations

An example of the effect of the procedure in the reduction of the initial interference in a handswab extract is shown in Figure 9. Obviously, an appreciable number of compounds remain, in this explosives-free sample, and these could probably be removed by more selective adsorbents. But the main objective so far has been the development of a screening procedure by which as many com-

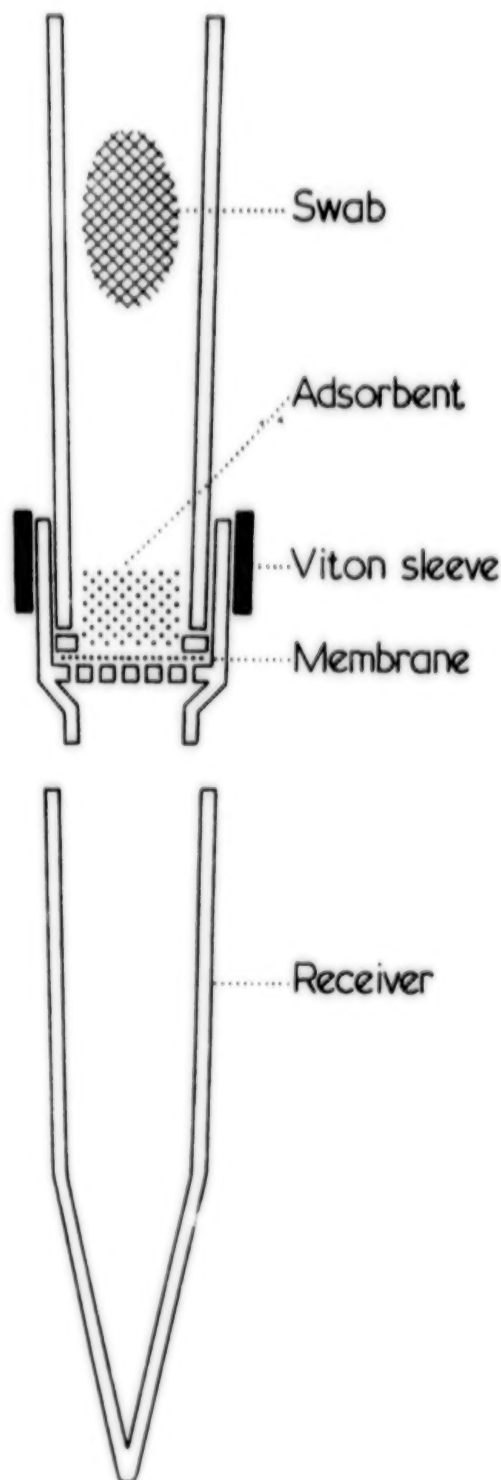


Figure 8. Centrifugal microfilter (Bioanalytical Systems) assembly for extraction and clean-up of hand swabs.

pounds as possible may be recognized. If more selective techniques are used, some of these are lost. It does in fact turn out that very few of the explosives components are overlapped by spurious



peaks, and most handswabs are at least qualitatively comparable in this respect.

The situation is exemplified in Figure 10 where, on a cleaned-up handswab extract I have superimposed a chromatogram due to 91 pg-amounts of each of 15 explosives components. This amount corresponds to 1 nanogram of each of them per swab. The only significant coincidences here are at the tetryl and the 2, 6-dinitrotoluene positions. I have collected about 100 swabs from people, the majority of who were employed in manual work,

26 mg PMDE

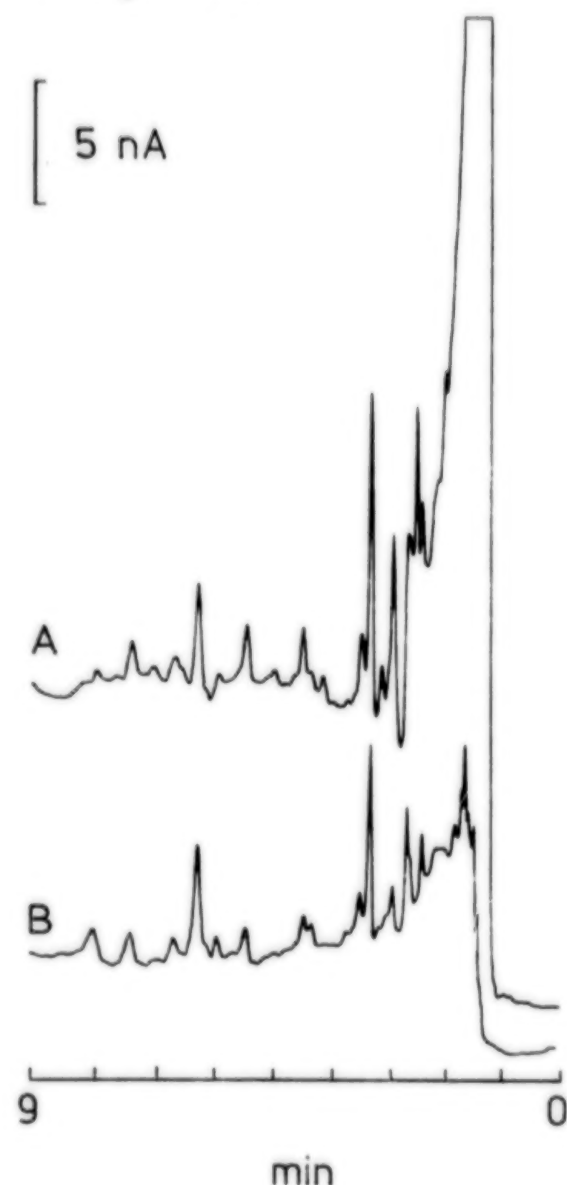


Figure 9. Chromatograms (PMDE) comparing hand swab extracts before (A) and after (B) clean-up.

and find that above the level of 1 nanogram/swab the only frequent significant overlaps are as Fig 10 indicates.<sup>4</sup>

Occasional overlaps occur with some other compounds, but with modified conditions it should be possible to exclude any possibility of confusion. I have examined the case of PETN specifically, with the result shown in Fig. 11. At a potential of -1.0 V a peak occurs at the PETN position in this particular handswab extract. But at a potential of -0.6 V the handswab peak virtually disappears, whereas the PETN peak is reduced only to a third of its original intensity. Similar experiments are applicable to other compounds.

Examples of chromatograms including an explosives-containing hand swab are shown in Figure 12. The hand swab was from a person who had

26 mg PMDE

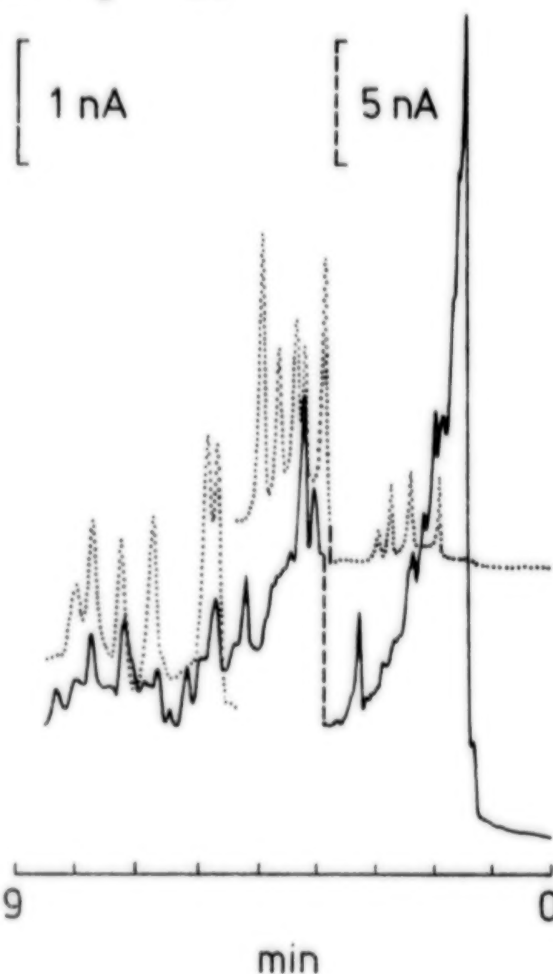


Figure 10. Handswab extract, with a superimposed chromatogram (PMDE) (dotted line) of 91 pg amounts of explosives components.

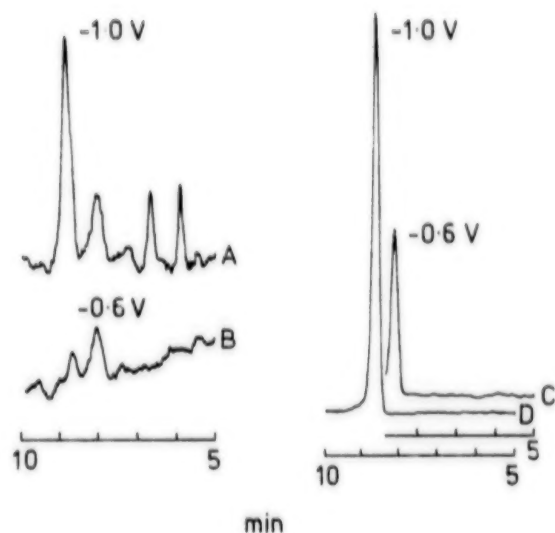


Figure 11. Chromatograms (PMDE) of a handswab extract (A and B) and PETN (C and D) with detection at  $-1.0$  V and  $-0.6$  V vs. Ag/AgCl.

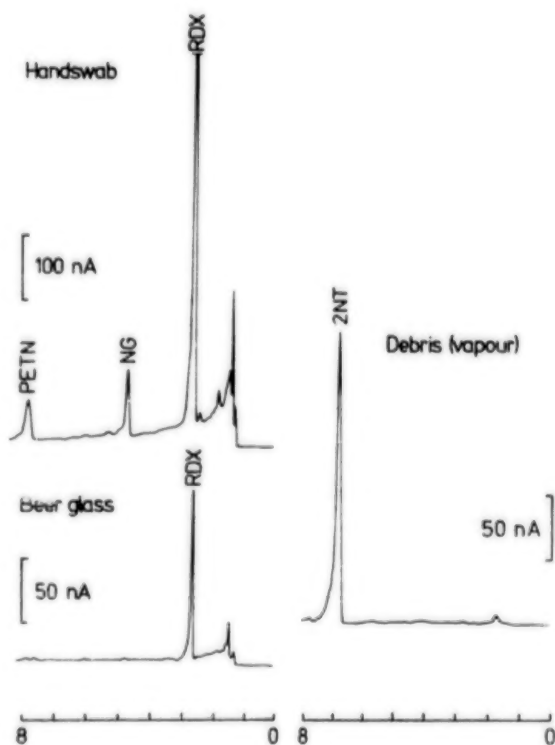


Figure 12. Examples of chromatograms (PMDE) from explosives-containing samples: Hand swab collected after 3 hours and an unknown number of handwashes following brief contact with Nobel-808, PE 4 and Cordtex; swab from a beer glass used  $2\frac{1}{2}$  hours and a hand-wash after PE-4 had been handled; and extraction assembly eluate after the vapour-sampling of debris containing *ortho*-nitrotoluene.

briefly handled wrapped cartridges of Nobel-808 and PE-4, and Cordtex detonating fuse. He was swabbed some 3 hours later, during which time he had washed his hands at least once. The chromatogram shows the presence, as expected, of RDX, NG and PETN, in amounts varying between 100–300 ng.

The other chromatograms (Figure 12) are from

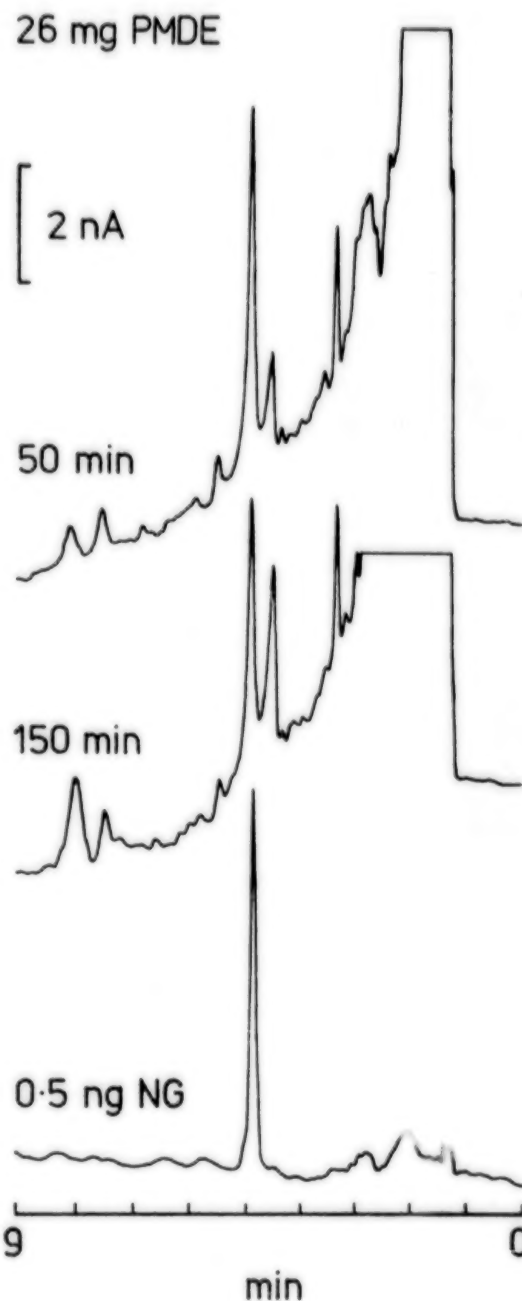


Figure 13. Chromatograms (PMDE) from handswabs collected at the indicated times after two shots had been fired from a Smith and Wesson model 10, .38 Special revolver.

a swab from a drinking glass used by a person who had handled PE-4 sometime earlier, and washed his hands—clearly RDX is present—and from an extract of the clean-up assembly after its use in a vapour sampling of some 1-day old debris left after the explosion of a simulated terrorist device containing ortho-nitrotoluene.

Figure 13 shows the results after a firearm had been discharged up to 2½ hours earlier. These chromatograms represent ca. 5% of the material present on the swab, and hence 6 ng after the longest time interval.

The lowest levels of NG detected so far are in the region of 0.2 ng/swab. This was in some work on cardiovascular tablets.<sup>5</sup> In the future it should be possible to increase this by an order of magnitude with the application of more specific clean-up techniques, as opposed to the general-purpose ones used here.

#### ACKNOWLEDGEMENT

I am indebted to the Editor of the *Journal of Chromatography* for permission to reproduce a number of the Figures.<sup>2,4</sup>

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# DETECTION AND ANALYSIS OF POLYNITROPHENOLS IN WATER BY REVERSED-PHASE ION-PAIR LIQUID CHROMATOGRAPHY

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**ABSTRACT.** The separation and quantitative analyses of mixtures of up to nine different polynitrophenols in water including both picric and styphnic acids by ion-pair liquid chromatography are described. Using Pic-A reagent (t-butyl ammonium phosphate) to produce the counter cation in methanol-water systems, quantitative results were obtained at phenol concentrations as low as 0.1 mg/liter (0.1 ppm). Details of a preconcentration step for the analyses of polynitrophenols at the parts per billion (ppb) level are given.

## INTRODUCTION

In the past, ammonium picrate (explosive D) has been widely used in a number of US Naval projectiles, but now its use has been largely discontinued. Subsequently, ordnance items containing ammonium picrate have become obsolete and were demilitarized either by burning or by containment in various dump sites. In May, 1979, the Bureau of Medicine and Surgery, Department of the Navy, in response to its Assessment and Control of Installation Pollutants (ACIP) programs at US Naval Stations, set a target interim maximum contaminant level (TIMCL) for nitrophenols including ammonium picrate and picramic acid at 0.001 mg/L (1 ppB). To this end, in order to assess the extent that ammonium picrate (more specifically, picrate ion) remains contained, it is essential that reliable methods be available to measure low level picrate and other nitroaromatic phenoxide ions in ground water.

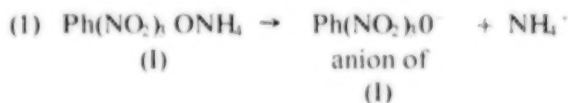
As a class, the polynitroaromatic phenols are quite acidic and possess  $pK_a$  values ranging from 0.23 (2,4,6-trinitrophenol or picric acid) to 4.5 (2-amino-4,6-dinitrophenol or picramic acid), and would be expected to exist almost entirely as the corresponding polynitrophenoxide anions in water. In addition, the salts of the polynitroaromatic phenols would be expected to be readily soluble in water. Ammonium picrate, for example is soluble to the extent of about five grams per liter in water at room temperature. Furthermore, picramic acid has recently been reported by Wy-

man et al to be a biotransformation product from picrate ion, while the formation of other compounds such as the isomeric dinitrophenols was suggested.

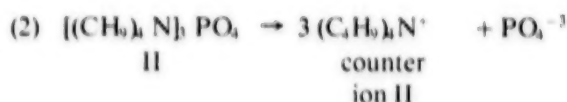
Recently, in an excellent review article, Tomlinson *et al.* outlined reverse phase ion-pair liquid chromatography (LC) as a method for the analyses of ionic species in water. In this review the authors cite the work of Culbreth *et al.* who describe a procedure for the analysis of 4-nitrophenol in the presence of 4-nitrophenol phosphate. It would appear then that ion-pair LC would be an excellent choice for the detection and analysis of various polynitroaromatic phenols in water. The objective of the present study, therefore, was to extend this ion-pair LC method for the analysis of picrate ion as well as other polynitroaromatic phenols at the parts per million (ppm) to the parts per billion (ppB) level in ground water.

## SIMPLIFIED PAIRED ION CHROMATOGRAPHY (PIC) THEORY

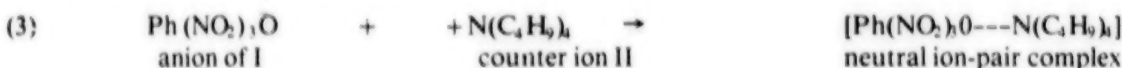
In this discussion, a simplified PIC theory will be illustrated for ammonium picrate. In the water sample to be analyzed, ammonium picrate (I) is completely ionized according to equation (1), where Ph represents a phenyl ring.



If tetrabutylammonium phosphate (II) (PIC reagent, Waters Associates) is incorporated in the LC eluent (usually methanol/water mixtures), it is also completely ionized according to equation (2).



On injection of the water sample into the LC, the anion of I forms a neutral ion-pair complex with the counter ion II according to equation 3.



Retention times of the polynitroaromatic phenols would be expected to vary with different substituents associated with the anion of I, thus making separations on the reverse phase (RP) column possible. In the absence of the PIC reagent, the polynitroaromatic phenoxide ions are not retained, hence not separated on the RP column.

## EXPERIMENTAL

### Polynitrophenol Solutions

All nitrophenols were purified by recrystallization from the appropriate solvents, and melting points compared with known literature values. 2,4,6-Trinitrophenol was also purified by recrystallization of its ammonium salt. Standard solutions of each nitrophenol varying from 15 to 350 mg/L were made by dissolving the nitrophenol directly in water and warming where necessary. Mixtures of nitrophenols were made from these standard solutions.

### Chromatographic Conditions

A high performance liquid chromatograph (Hewlett-Packard, Model 1084A) equipped with a variable wavelength detector (HP Model 1030), variable volume injector, built-in processor for full integration calculation and printer-plotter capability was used with a 10 micrometer particle size RP-8 column, 25 cm long and 4.6 mm ID, maintained at 40°C. Unless stated otherwise, detector wavelength was 254 nm.

## RESULTS AND DISCUSSION

For isocratic elution (Table 1), column flow was 2.0 ml/min; mobile phase, 50/50 methanol/water, by volume, containing  $5 \times 10^{-3}$  M tetrabutylammonium phosphate reagent buffered at pH 7.5 (PIC A reagent, Waters Associates). Two bottles (30 mls) of PIC A reagent were dissolved in one liter of distilled water, diluted with another liter of HPLC grade methanol, and filtered through a 0.45 micron filter (Millipore). The solvent was di-

vided between reservoirs "A" and "B" of the chromatograph and degassed for one half hour at 35°C before establishing column flow.

For gradient elution (Table 2) column flow was 1.0 ml/min of a 45/55, by volume, mixture of methanol/water containing  $5 \times 10^{-3}$  M tetrabutylammonium phosphate reagent for 11 minutes then increased to 50/50, by volume, methanol/water from 11 to 16 minutes. The mobile phase for gradient elution was prepared by dissolving 15 mls of PIC A reagent in one liter of distilled water, filtering through a 0.45 micron filter, and placing the filtrate in reservoir "A". Reservoir "B" was filled with a solution made by dissolving 15 mls of PIC A in 100 mls of distilled water and diluting with 900 mls of HPLC grade methanol. Both solutions were degassed at 35°C for one half hour before establishing column flow.

The RP-8 column was dedicated solely for the use with PIC A reagents and was thoroughly rinsed with methanol/water, 50/50, by volume, and allowed to stand in distilled water at the end of each day.

### Variable Wavelength Analyses

In aqueous solutions buffered at pH 7.5, 2-amino-4,6-dinitrophenol has two maximum absorptions at 310 nm and 410 nm, while, 2,4,6-trinitrophenol exhibits a single maximum at 355 nm. These maxima were not found to shift in the presence of  $5 \times 10^{-3}$  M tetrabutylammonium phosphate. Liquid chromatographic separations of these polynitrophenols were made with detector wavelength settings at 254 nm, 310 nm, 355 nm, and 410 nm. Area and peak height response were measured at each wavelength. Detector responses for 2-amino-4,6-dinitrophenol at 310 nm and 410 nm were found to be 0.81 and 0.91 times the response at 254 nm, respectively. Detector responses for 2,4,6-trinitrophenol at 355 nm were 1.3 times the response at 254 nm. At wavelengths lower than 230 nm, absorption interferences of the solvent mobile phase were observed. Although no sub-

**Table 1. VARIATION OF RETENTION TIMES AND DETECTOR RESPONSES IN THE ANALYSES OF POLYNITRO-PHENOLS IN WATER BY ION-PAIR LIQUID CHROMATOGRAPHY**

Phenol <sup>a</sup>	Retention <sup>b</sup> Time, min	Detector Response <sup>c</sup>	
		Area Counts/ng	mm/ng <sup>d</sup>
(water)	1.5	—	—
2-amino-4,6-dinitro-	3.06	133 ± 3 (8)	1.56 ± 0.04 (8)
2,4-dinitro-	4.26	104 ± 2 (8)	0.86 ± 0.02 (8)
2-methyl-4,6-dinitro-	6.34	92 ± 4 (8)	0.54 ± 0.01 (8)
2,4,6-trinitro-	7.67	103 ± 2 (6)	0.51 ± 0.01 (9)
3-methyl-2,4,6-trinitro-	11.5	89 ± 3 (6)	0.30 ± 0.01 (8)

(a) Concentration range, 1 to 15 mg/L in water; 100 microliter injection.

(b) Isocratic elution; mobile phase, 50/50 methanol/water, by volume, containing  $5 \times 10^{-3}$  M tetrabutylammonium phosphate buffered at pH 7.5; flow, 2.0 ml/min; RP-8 column, 10 micrometer particle size, 25 cm × 4.6 mm ID.

(c) Detector wavelength, 254 nm; values in parentheses are number of determinations; ± values are standard deviations for the detector responses observed.

(d) Height sensitivity,  $8 \times 10^{-5}$  AU/mm.

stantial changes in detector responses were observed at wavelengths other than 254 nm, the measurable differences in response factors at these different wavelengths could serve as a positive means of compound identification.

#### Detection Limits

In order to be able to *detect* a particular nitrophenol in water, the sample signal must be at least twice the noise level at any given detector sensitivity. From Table 1, the height response for 2-amino-4,6-dinitrophenol was found to be 1.56 mm/ng at a detector sensitivity of  $8 \times 10^{-5}$  AU/cm, where the noise level was ± 1 mm. Therefore, the sample peak height must be at least

2 mm which corresponds to 1.3 ng, and for a 100 microliter injection is 0.013 mg/L (lower detection limit for 2-amino-4,6-dinitrophenol). Since the height response for 2,4,6-trinitrophenol is 0.51 mm/ng under the same conditions, the detection limit of this nitrophenol may be calculated to be 0.040 mg/L (lower detection limit for 2,4,6-trinitrophenol).

#### Preconcentration and Analysis at the Parts Per Billion (ppB) Level

At first, an extraction scheme appeared attractive, whereby the nitrophenol would be extracted from the water sample after pH adjustment into a small volume of benzene, and then back-extracted

**Table 2. SEPARATION OF AN AQUEOUS NINE COMPONENT POLYNITROPHENOL MIXTURE BY ION-PAIR LIQUID CHROMATOGRAPHY**

Phenol Mixture <sup>a</sup>	Retention <sup>b</sup> Time, min	Relative Detector Response <sup>c</sup>	
		Area Counts/ng	mm/ng
water	3.0	—	—
3-hydroxy-2,4-dinitro-	5.32	0.44	0.49
3-hydroxy-2,4,6-trinitro-	6.11	0.44	0.55
2-amino-4,6-dinitro-	7.13	1.0 <sup>d</sup>	1.0 <sup>e</sup>
3-hydroxy-4,6-dinitro-	8.52	0.32	0.28
2,6-dinitro-	9.46	0.79	0.57
2,4-dinitro-	10.5	0.79	0.50
2-methyl-4,6-dinitro-	16.8	0.69	0.31
2,4,6-trinitro-	20.0	0.78	0.39
3-methyl-2,4,6-trinitro-	25.8	0.69	0.29

(a) Compounds present in concentration range, 2 to 6 mg/L; 100 microliter injection.

(b) Elution conditions: isocratic for 11 min; flow 1.0 ml/min; mobile phase 45/55 methanol/water, by volume, then gradient elution to 50/50 methanol/water from 11 to 16 min, then isocratic to 30 min. RP-8 column, 25 cm × 4.6 mm ID, 10 micrometer particle size; mobile phase containing  $5 \times 10^{-3}$  M tetrabutylammonium phosphate at pH 7.5.

(c) Detector wavelength, 254 nm.

(d) Detector response, 255 area counts/ng.

(e) Detector response, 1.63 mm/ng at a sensitivity of  $8 \times 10^{-5}$  AU/cm.



from the benzene into another small volume of water containing sodium bicarbonate prior to LC analysis. However, the distribution coefficients of the nitrophenols between benzene and water at a given pH were not large enough to effect a real concentration of 100 to 1 or 50 to 1. The distribution coefficients of 2-amino-4,6-dinitrophenol and 2,4,6-trinitrophenol between benzene and water were determined to be 31 (at pH 2.5) and 52 (at pH 1.3), respectively. In addition, there was another complication. At pH values lower than pH 2, the amine group of 2-amino-4,6-dinitrophenol became protonated in water and was not extracted by benzene.

Another attempt was made to concentrate the polynitrophenol on a Bondapak C-18 Porasil Sep Pak (Waters Associates) cartridge. Fifty to one hundred milliliters of an acidified water sample (pH adjusted to 2.5) containing a 1 ppB mixture each of picrate and picramate ions was passed in increments through the cartridge. The cartridge was then extracted with 2.0 ml of HPLC methanol and the methanol extract was evaporated to a measured volume of approximately 0.5 ml prior to LC analysis. Although some concentration of the nitrophenols was achieved with this procedure, overall recoveries of the nitrophenols were only around  $60 \pm 10\%$  at the 1 ppB level. This is undoubtedly due to the marked tendency of both nitrophenols to ionize and to be "washed" off the C-18 cartridge.

Another method, currently under investigation, appears to be superior. One milliliter of PIC A reagent was added to 100 mls of the aqueous sample to be analyzed, and then the mixture was extracted with 10 mls of methylene chloride. By this procedure, essentially 100% of the polynitrophenol was extracted into the methylene chloride as the neutral ion-pair complex. The methylene chloride was then carefully evaporated to dryness, and the residue taken up in 0.40 ml of methanol/water, 50/50, by volume, containing phenolphthalein as an internal standard. Using this method, picrate ion has been analyzed at the 0.6 to 1.0 ppB level with an overall recovery of  $103 \pm 15\%$ .

The procedures outlined here can be readily used with most conventional liquid chromatographs employing the usual standard 254 nm UV

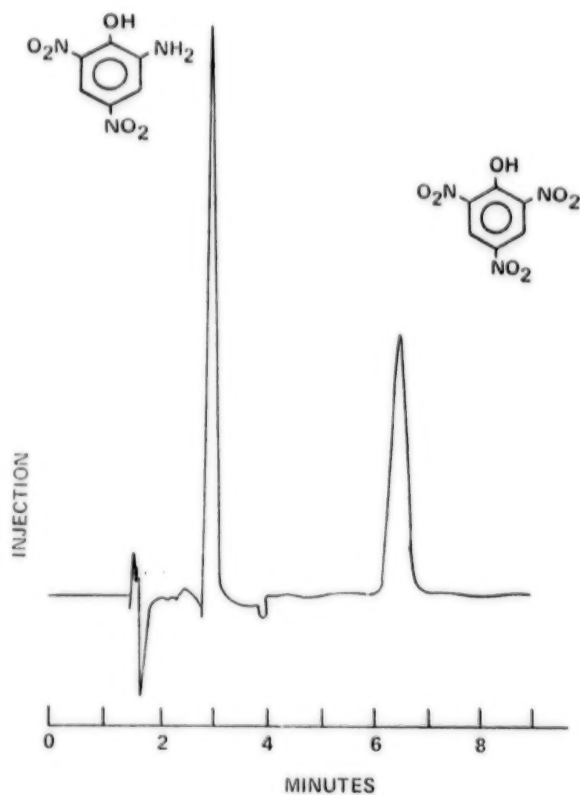


Figure 1. PIC Separation of 2-Amino-4,6-Dinitrophenol (Picramic Acid) and 2,4,6-Trinitrophenol (Picric Acid) at 1 PPM Level.

detector for the analyses of polynitroaromatic phenols at the ppB level with a simple preconcentration step. It may be possible, however, with more sophisticated detectors such as the thermal energy analyzer (TEA) detector or by a phosphorescence spectroscopic technique, that these ppB levels could be reached directly without a preconcentration step.

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# LIQUID CHROMATOGRAPHY/ELECTROCHEMISTRY DETERMINATION OF EXPLOSIVES: IMPROVED PERFORMANCE USING LOW DEAD VOLUME MULTIPLE ELECTRODE TRANSDUCERS

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**ABSTRACT.** Most commonly used explosive substances are electrochemically reducible at modest negative potentials (below  $-1.0$  volt vs. Ag/AgCl). As a result, electrochemistry provides excellent selectivity for these substances because very few naturally occurring materials contain nitro groups. The combination of reverse phase chromatography with electrochemical detection therefore provides a unique opportunity to determine very small amounts (typically 1 ng) of various explosive substance. In this presentation, the principles and experimental practice of LCEC will be reviewed with specific reference to optimization of the quantitation and identification of individual explosive materials. A series dual-electrode scheme was applied to the detection of explosive compounds in standards, gunshot residue and environmental samples. The series dual-electrode thin-layer transducer can extend the specificity and detection limits (for compounds reduced at higher energies) of the amperometric detector and can also provide better assurance of peak identity. In the case of polynitro aromatic explosives, the detection limits obtained with the dual-electrode transducer (signal measured at the downstream electrode) were higher by a factor of 3-4 than with a single electrode transducer because the decrease in the baseline noise did not fully compensate for the decrease in the electrolysis current at the downstream electrode. Operating the reductive LCEC system with a series dual-electrode transducer allows a direct injection of the sample solution without the need to remove dissolved oxygen prior to the injection. The described methodology permits detection of explosive compounds at detection limits below 10 ppb, depending on the particular compounds. LCEC appears to have significant advantages vs. gas phase techniques for the determination of nitro-based explosives for environmental and forensic purposes. The primary future direction is to improve reliability for the occasional user of the technique. When large numbers of samples need to be processed on regular basis, the method is well established and few problems are encountered with dedicated instrumentation.

## INTRODUCTION

The first practical liquid chromatography/electrochemistry (LCEC) experiments were carried out in early 1972. The technological developments followed the need to solve an important problem in neuropharmacology. Determination of catecholamine and serotonin neurotransmitters in brain tissue using such diverse techniques as fluorescence, gas chromatography/mass spectrometry, and various radiochemical techniques left much to be desired. LCEC appeared to be a good solution to some of the problems and after a decade of de-

velopment, nearly a thousand publications have appeared. The primary attributes of the technique are its good selectivity, low detection limits, wide applicability (especially vs. fluorescence), and low cost (especially vs. GCMS and radiochemical procedures).

In recent years a number of new applications (enzyme activity measurements, GABA, acetylcholine, NADH, pterins, explosives etc.) have been developed. Multiple-electrode LCEC detection systems are now available which permit significantly improved performance. The new trans-

ducers are compatible with short, high speed columns and longer microbore columns. With multiple electrode LCEC the identification of individual substances can be confirmed and the selectivity can be much improved. In addition, better detection limits can be achieved for some compounds. The latest developments in LCEC technology will be briefly described with respect to (1) multiple working electrodes, (2) "high speed" columns, and (3) post-column reactions. All three areas provide opportunities for further application of LCEC to explosives.

### ELECTROCHEMISTRY OF EXPLOSIVE SUBSTANCES

LCEC of reducible substances is now very highly developed and is in widespread use for a variety of substances [Shoup (1982); Bratin, Kissinger, and Bruntlett (1981)]. A large percentage of the applications for reductive LCEC have involved nitro compounds which are generally well behaved electrochemically. Nitro aromatic, nitramine, and nitrate ester explosives are all good LCEC candidates. In the late 1970's our laboratory at Purdue began an extensive study of the potential use of LCEC for monitoring explosives in gun shot residue, post-blast debris, environmental samples, and biological fluids. Much of the early work has been summarized in the literature [Bratin, Kissinger, Briner, and Bruntlett (1981)] and will not be reported here. Several groups (see other papers in this volume) have continued this effort and it is now clear that LCEC is a very viable approach to determination of explosives in many situations. The primary difficulty with the technique relates to the lack of education of the forensic science community in electrochemical methods. Perhaps equally important is that few laboratories encounter enough samples to keep the instrumentation in constant use, a requirement for reliable and cost effective operation.

### MULTIPLE ELECTRODE LCEC

Electrochemistry in thin layers of solution is a very highly developed field of electroanalytical chemistry. The thin-layer geometry is ideal for LCEC in that it provides a very low volume transducer which can faithfully reproduce the shape of concentration profiles ("peaks") eluting from very efficient LC columns. Figure 1 illustrates the most popular LCEC detector cell. The thin-layer channel is defined by a gasket held between the

upper block (a stainless steel auxiliary electrode with low dead volume fittings) and the lower block (an inert polymeric material containing one or more working electrodes at which the reactions of interest occur). The effective dead volume can be made less than 1  $\mu$ L, a very difficult task for optical detectors. Routine determination of 1 pmole of an analyte is generally very straightforward and often 0.1 pmole or less can be quantitated in optimized procedures.

The simultaneous use of two working electrodes greatly improves both the qualitative and quantitative aspects of an LCEC experiment. Electrodes of the same or different materials may be used and the electrode potentials may be independently controlled. In the "parallel mode" the compounds eluting from the column pass over each electrode at the same time. The following applications are quite useful:

1. The ratio of currents monitored at each electrode can provide confirmation of peak identity and purity.
2. Oxidations and reductions can be carried out simultaneously. This saves time and enhances selectivity. This can be ideal for compounds present in several different redox states (*e.g.* pterins).
3. Signals from low and high potential reactions can be recorded simultaneously, providing both greater selectivity and wider applicability in a single experiment.
4. A difference signal can be plotted to subtract out "common mode" information while enhancing

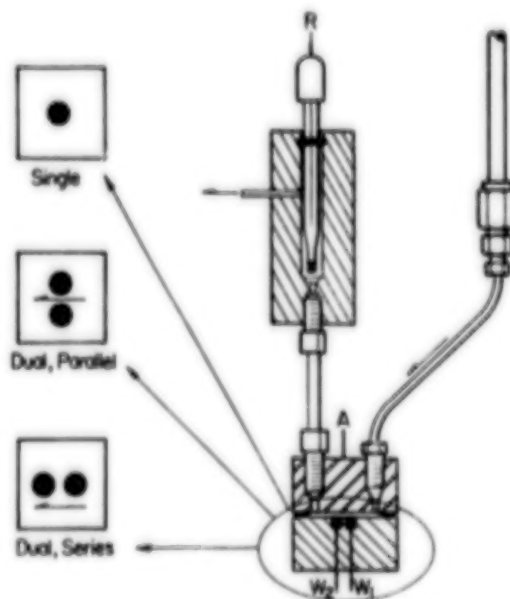


Figure 1. Thin-Layer Amperometric Detector Cell.

ing detection of the desired compound.

In the "series mode" the lower block is rotated 90° in relation to the flow stream. Products of the upstream electrode reaction can be detected downstream. If an oxidation is carried out upstream a reduction is accomplished downstream and vice versa. The following applications are popular:

1. The ratio of currents monitored at each electrode can provide confirmation of peak identity and purity.
2. Selectivity is enhanced at the downstream electrode because compounds with chemically irreversible reactions upstream are discriminated against.
3. The upstream electrode can "derivatize" compounds to enhance detectability at the downstream electrode. Overall selectivity and detection limits can be greatly improved.
4. Dissolved oxygen can be discriminated against, simplifying LCEC of compounds that ordinarily would require mobile phase deoxygenation (e.g. nitro compounds).
5. "Common mode" currents can be discriminated against by taking the difference between the two signals.

Both series and parallel dual electrode LCEC provide many opportunities for study of explosives because of the wide range of redox properties involved, including some compounds that are relatively difficult to reduce (e.g. nitramines, nitrate esters) and some that reduce extremely easily (e.g. picric acid).

### "HIGH SPEED" COLUMNS FOR LCEC

Short LC columns (typically 3-10 cm) packed with small particles (typically 3µm) can provide very high resolution separations in a few minutes. For example, Figure 2 illustrates the separation of 17 neurochemicals in under 8 minutes using an experimental 10 cm reverse phase column. This technology requires modification of a conventional LCEC system to minimize dead volume, but these modifications are quite straightforward and present no unusual problems [Shoup (1983)]. This development presents a great opportunity for solving certain types of problems, but by no means replaces LCEC experiments using more conventional 25-30 cm columns. With respect to explosives, short high speed columns afford detection limits below 0.1 pmole, however, in our experience it is rare that such low detection limits are necessary for forensic work. Nevertheless, work at the 1

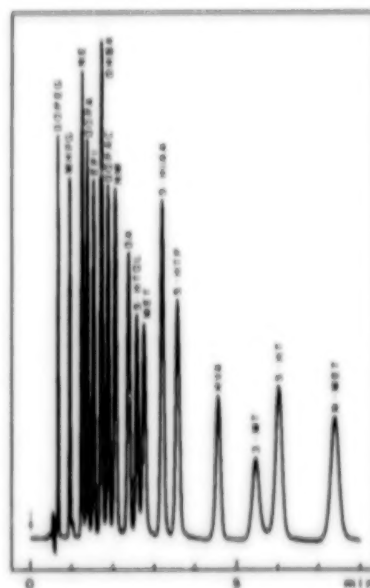


Figure 2. Separation of neurochemical standards.

pmole level has become extremely reliable for routine purposes.

### POST-COLUMN REACTIONS IN LCEC

Post-column chemical reactions coupled to electrode reactions are also expanding the range of LCEC applications. Figure 3 illustrates four con-

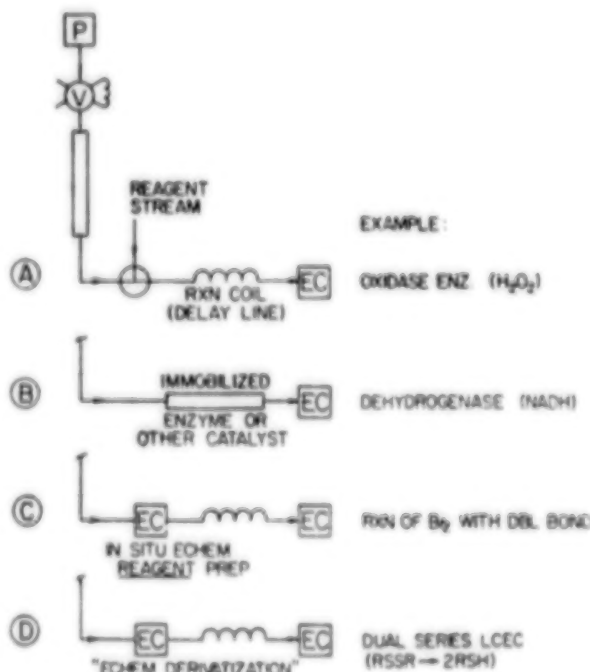
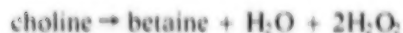


Figure 3. Post-column strategies for LCEC.

figurations. In *A* a reagent is added, mixed, and reacted in a delay line followed by electrochemical detection. A superb example of this is the determination of acetylcholine in brain tissue by reverse-phase LCEC. Acetylcholine esterase and choline oxidase are mixed in and the detection process proceeds as follows:



The peroxide is detected electrochemically at a platinum electrode [Potter, Meek, and Neff (1982)].

In *B*, a catalyst in immobilized and a cofactor is detected. For example, using a dehydrogenase enzyme an alcohol can be detected indirectly by monitoring the turnover of NAD to NADH, the latter being ideal for electrochemical detection. In *C* an upstream electrode generates a reagent (e.g.  $\text{Br}_2$  from  $\text{Br}$  in the mobile phase) which reacts with a nonelectroactive compound (e.g. an unsaturated fatty acid) and the decrease in reagent concentration is monitored downstream. In *D*, the analytes of interest are converted at an upstream electrode into a product which is more selectively detected downstream. Examples include reduction of a nitro compound to a hydroxylamine, reduction of a disulfide to a thiol, and reduction of a nitrate ester explosive to generate the nitrite ion. In all three examples, the reduction product is detected by oxidation and the resulting anodic current is used for quantitation of the original material.

It was the intention of this brief review to indicate that LCEC technology is advancing rapidly. The technique is far more reliable and now exhibits significantly better sensitivity and detection

limits. When coupled with pre- and post-column reactions the range of applicable compounds has been dramatically increased. The improvements enhance our original publication on LCEC of explosives [Bratin et. al (1981)], but do not invalidate any aspect of our earlier work. The principles and applications of LCEC have been thoroughly reviewed in recent text [Kissinger (1984)].

#### ACKNOWLEDGEMENT

The author wishes to thank Dr. Ron Shoup and his group at Bioanalytical Systems R&D for their continuous input of new ideas. Prof. LeRoy Blank of the University of Oklahoma is thanked for his contribution of Figure 2 and the innovative work that made it possible.

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**CHARACTERISTICS OF PLASTICS, POLYMERS  
AND EXPLOSIVES BY DIRECT SIZE  
EXCLUSION CHROMATOGRAPHY**

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Waters Associates

**Paper No. 5 not submitted for publication.**

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## **GENERAL ANALYSIS**

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# IDENTIFICATION OF REACTION PRODUCTS IN RESIDUES FROM EXPLOSIVES

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**ABSTRACT.** Reaction products and unreacted components in explosive residues have been identified in test explosions of: (i) "home-made" explosive mixtures of oxidisers and fuels, (ii) high explosives of the "water-gel" type. The "home-made" explosives were two-component mixtures of oxidisers (chlorates, perchlorates, nitrates) with fuels (sugar, sulphur, aluminum) and were ignited both confined and unconfined. The high explosives were sticks of "water-gel" explosive produced by two different manufacturers. The composition of residues from these explosives was compared to residues from dynamite. Residues were systematically analysed by routine solvent extraction methods and analytical procedures.

Previous work (Beveridge *et al.* (1975)) has described the analysis and identification of residues from the explosion of dynamites, plastic explosives and some chemical mixtures, primarily smokeless powders. This work extends the explosives studied to the "water-gel" type of high explosive and to a wider range of "home-made" chemical mixtures.

The objective of this work was two-fold: to expand our analytical data base (Beveridge, (1978)) and hence improve interpretation of casework analyses, and to continue testing the effectiveness of the analytical scheme for explosive residues.

## EXPERIMENTAL

### Chemical Mixtures

Chemicals used were reagent grade sodium chlorate, sodium nitrate, potassium chlorate, potassium perchlorate, potassium nitrate, calcium nitrate, sulphur, aluminum powder and charcoal. Domestic table sugar was used for sucrose. The chemicals were carefully ground by hand prior to mixing.

Burning was carried out on both confined and unconfined mixtures. Unconfined burning was conducted in an evaporating dish in a fume hood using a nitrocellulose-based fuse for initiation.

Confined burning was conducted at an explosives range using ca. 70g of chemicals in steel pipes (4-5 inches long, 1 inch inside diameter, 1/8 inch

wall thickness) with threaded end-caps. One end-cap had a 1/8 inch hole through which were inserted the wires of the initiator, an electric squib. The confined burns were conducted in steel cylinders (1-2 feet diameter, 0.5-1 inch wall thickness) with flat circular caps (2 inches thick) on top and bottom. This permitted satisfactory recovery of pipe fragments. The cylinders were washed with water and acetone between tests. Residue recovery was restricted to the pipe fragments, using solvent extraction (acetone and water).

### "Water-gel" Explosives

Explosives used were "Powermex 500", manufactured by Canadian Industries Ltd., and "Tovex 5000 SD", manufacturer by Du Pont. Each explosive was an aluminised gel in a plastic tube.

Initiation was by No. 6 electrical blasting cap. Residues were collected from various surfaces including wood, cloth and steel.

### Methods

The scheme used in the analysis of the explosives and their residues was the systematic application of solvent extraction, microscopy, infrared spectroscopy (IR), thin-layer chromatography (TLC), X-ray diffraction (XRD), emission spectroscopy (ES) and chemical tests as reported previously in detail (Beveridge *et al.* (1975)). For certain applications, other methods have been

added—a scanning electron microscope with energy dispersive X-ray analyser (SEM/EDX) for qualitative elemental analyses (including chlorine and sulphur), and gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) of trimethyl silyl (TMS) ether derivatives of sugars.

#### SEM/EDX

A Semco (Bausch & Lomb) Nanolab 7 SEM equipped with a Kevex 7000/77 Energy Dispersive X-ray spectrometer was used.

#### Gas Chromatography

N-trimethylsilylimidazole in pyridine, marketed by the Pierce Chemical Company as TRI-SIL 'Z'<sup>®</sup>, was used to silylate sugars in order to facilitate analysis by gas chromatography. The standard reaction conditions supplied by the manufacturer were used. One milliliter of TRI-SIL 'Z'<sup>®</sup> was added to 15 milligrams of the sugar standards glucose, fructose and sucrose and to 50–100 milligrams of aqueous extracted residues. The reactions were conducted in "Reactivials"<sup>®</sup>. The samples were heated to 60–70°C for approximately 45 minutes or until the sugar had dissolved.

GC analysis was performed on a Perkin Elmer model 900 gas chromatograph equipped with flame ionization detectors, using a 12 foot x 1/8 inch stainless steel column packed with 3% OV-1 coated on 80/100 mesh Chromasorb W(HP).

#### Gas Chromatography/Mass Spectroscopy (GC/MS)

A Finnigan model 3100 quadrupole/mass spectrometer interfaced to a Finnigan 9500 gas chromatograph was used. The mass spectrometer was operated at 70 eV. The GC contained a 6 foot by 1/8 inch glass column packed with 3% OV-1 on 80–100 mesh Chromasorb W(HP).

### RESULTS AND DISCUSSION

#### (a) Chemical Mixtures

The mixtures were, with two exceptions, two-component combinations of oxidisers (perchlorate, chlorate, nitrate) with fuels (sucrose, sulphur, aluminum) which were burned unconfined, and confined in pipes. Appendix "A" provides details of the specific mixtures used and the complete analytical results.

The study focussed on the condensed reaction products formed by each oxidiser and fuel. The reaction product compositions were found to be in-

dependent of the degree of confinement. These results are summarised in Table 1. The principal observations made during the tests are described, firstly for the oxidisers and then for the fuels.

TABLE 1. CONDENSED REACTION PRODUCTS FROM BURNING OF OXIDISER/FUEL MIXTURES

Oxidiser	Condensed Reaction Products
Perchlorate ( $\text{ClO}_4^-$ )	Chloride ( $\text{Cl}^-$ ) (major product) Chlorate ( $\text{ClO}_3^-$ ) (minor product)
Chlorate ( $\text{ClO}_3^-$ )	Chloride ( $\text{Cl}^-$ )
Nitrate ( $\text{NO}_3^-$ )	Nitrite ( $\text{NO}_2^-$ )
Fuel	
Sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ )	Carbonate ( $\text{CO}_3^{2-}$ ) Bicarbonate ( $\text{HCO}_3^-$ )
Sulphur (S)	Sulphate ( $\text{SO}_4^{2-}$ )
Aluminum (Al)	Aluminum Oxide ( $\text{Al}_2\text{O}_3$ )

#### (i) Perchlorates

The perchlorates underwent a rapid and intense reaction with each of the fuels used. When confined, the reactions shattered the pipes into small fragments.

The major reaction product, produced in high yield, was the alkali metal chloride, identified by XRD. Also, a small quantity of chlorate was produced and was identified, along with traces of unreacted perchlorate, by IR and XRD (Appendix "A", nos. 1 & 2).

#### (ii) Chlorates

Like the perchlorates, the chlorates reacted vigorously with each of the fuels. The confined reactions split the pipes longitudinally, but produced less fragmentation than did the perchlorates. The only product recovered was a high yield of alkali metal chloride, identified by XRD (Appendix "A", nos. 3 thru 6).

#### (iii) Nitrates

In binary mixtures, nitrates reacted less violently with the fuels than did the perchlorates or chlorates. When confined, the damage to the pipe was limited to blowing a hole in, or blowing off, one end cap. The reaction product was nitrite, identified by spot test and by IR (Appendix "A", nos. 7 & 8). Attempts to burn a calcium nitrate mixture were unsuccessful due to its highly hygroscopic nature (Appendix "A", no. 9).

In a ternary mixture with sulphur and charcoal (black powder), burning of the confined mixture split the pipe longitudinally and produced damage similar to chlorate binary mixtures. The principal reaction product was nitrite (Appendix "A" nos. 10 and 11).

#### (iv) Sucrose

In the pure dry state, sucrose was readily identified by XRD, IR or the polarising microscope. However, evaporation of aqueous extracts of residues containing sucrose tended to yield syrups rather than solids, requiring an alternate method for identification. Formation of the trimethylsilyl ether derivatives (TMS) of sucrose, which were analysed and identified by gas chromatography/mass spectrometry (GC/MS), was found to be a suitable procedure. One interesting facet of the sucrose reactions was the identification, by the TMS-GC method, of glucose and fructose in the residue from the unconfined burning of potassium perchlorate and sucrose. No condensed reaction product was observed, and it seems more likely that these monosaccharides were produced by hydrolysis of the sucrose on extraction rather than by the burning reaction (Appendix "A" no. 2).

The nature of the reaction products of sucrose was dependent on the oxidiser used. When burned with chlorates and perchlorates, sucrose produced virtually no condensed reaction product. In these reactions, the product was principally the alkali metal halide, and thus was derived almost entirely from the oxidiser with chlorate only, a spot test indicated the possible presence of carbonate or bicarbonate, but neither could be confirmed by IR or XRD (Appendix "A" nos. 3, 4).

On the other hand, when burned unconfined with nitrates, the sucrose produced a major proportion of the condensed reaction product. In two separate reactions of potassium nitrate and sucrose, the reaction products obtained were potassium carbonate and potassium bicarbonate (identified by XRD and IR) along with nitrite (Appendix "A" nos. 7, 8).

#### (v) Sulphur

The principal reaction product of sulphur when burned with an oxidiser was sulphate. This was identified by IR or XRD (Appendix "A", nos. 5, 10, 11).

The composition of the solid formed by evaporation of solutions containing carbonate and sulphate ion was dependent on the cation. XRD showed that potassium sulphate and carbonate were recovered unchanged from aqueous solution. With the sodium salts, however, when the mole ratio of sodium carbonate to sulphate was in the range 0.2 to 0.5:1, the solid isolated by evaporation was identified by XRD as sodium carbonate sulphate  $(\text{Na}_2\text{CO}_3)_n(\text{Na}_2\text{SO}_4)_{1-n}$  ( $n = 0.2$  to  $0.5$ ). This compound and its formation were discussed

in previous work with respect to aqueous extracts of dynamite residues (Beveridge *et al.* (1975)).

In this study, sodium carbonate sulphate was identified by XRD as the product of aqueous extraction of residue from the unconfined burning of the ternary mixture of sodium nitrate, sulphur and carbon. Prior to aqueous extraction, XRD of the residue showed it to be a carbonate-stabilised form of sodium sulphate (Beveridge *et al.* (1975)). That is, the product of aqueous extraction did not have the same X-ray diffraction pattern as the unextracted residue.

That certain dynamites and sodium nitrate-based black powders can produce residues with the same composition should not be a practical problem in determining the type of explosive used if the nature of the explosion can be inferred from the damage, fragmentation, etc. If the residue were to be dealt with in isolation, however, then dynamite which contains sulphur and sodium nitrate, and sodium nitrate-based black powder would have to be given equal consideration as possible sources (Appendix "A" no. 11).

#### (vi) Aluminum

The predicted product of the reaction of aluminum with oxidising agents is aluminum oxide. However, in only one instance ( $\text{KCIO}_4/\text{Al}$  burned unconfined) was aluminum oxide identified by XRD in residue. In every test involving aluminum, regardless of the stoichiometry of the mixtures, unreacted aluminum was recovered (Appendix "A" nos. 1, 6).

#### (b) "Water-Gel" High Explosives

"Water-gel" high explosives, or "cap-sensitive slurries" are high explosives, based on ammonium nitrate, which can be initiated by a blasting cap. Like dynamite, they are distributed in "stick" form, but do not contain explosive oils such as nitroglycerine. They may, however, contain components in common with dynamites, *e.g.* sodium nitrate and ammonium nitrate. Our studies on residues from dynamite showed that aqueous extraction yielded principally sodium salts. If the dynamite contained sulphur, the product was sodium sulphate or sodium carbonate sulphate. If there was no sulphur in the formulation, the product was sodium carbonate accompanied by nitrite (Beveridge *et al.* (1975)).

Thus, it was of interest to determine the reaction products formed by the "water-gel" high explosives and to determine if the "water-gel"



residues could be distinguished from dynamite residues.

Two explosives produced by different manufacturers were selected. The detailed results of the analyses are given in Appendix "B". The main points arising from the tests are discussed for each explosive.

(i) "Tovex 5000-SD"

The major components of the explosive were monomethylamine nitrate (MMAN), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), sodium nitrate ( $\text{NaNO}_3$ ) and aluminum (Al).

Each test explosion led to recovery of a large quantity of aluminum flakes. However, no unreacted explosive (a pink aluminised gel) was recognised in any debris. In two of the explosions, the identification of MMAN by IR (Parker, (1975)) along with unreacted sodium nitrate, aluminum and a nitrite reaction product, served to identify the source of the residue as a "water-gel" high explosive of the "Tovex" type (Appendix "B" nos. 13 & 14). In two other explosions, the residue components identified were sodium, nitrate, aluminum and, in one instance, carbonate. In case-work, this residue would have been described as originating from any aluminised high explosive containing sodium nitrate—which could include many slurries and "water-gels" and possibly some less common dynamites.

Identification of MMAN in "Tovex" residue is therefore most important to narrow down the possible sources of the original explosive. Its very characteristic infrared spectrum is our preferred method of identification. MMAN has been recovered from both acetone and water extracts. Contrary to a published report (Parker (1975)) we have not observed MMAN to be unstable in acetone, and therefore have found no reason to change from acetone to methanol for extraction of this type of explosive. This aids extraction of "unknown" residues, since the normal sequence of ether-acetone-water may continue to be used without risk of decomposing MMAN.

(ii) "Powermex 500"

Two "Powermex-500" compositions were used—one with sodium nitrate as a major component, and one which contained no significant amount of sodium nitrate. The other major components were ethylene glycol mononitrate (EGMN), calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ), ammonium nitrate and aluminum.

This was our first test of an explosive containing calcium nitrate, a white hygroscopic solid which

has a stable tetrahydrate form and which is readily soluble in acetone and water. In an extraction sequence of ether-acetone-water it is, therefore, likely to be found in the acetone extract. Hence, acetone extracts should be screened for calcium ions as well as for nitrate and ammonium.

In two test explosions of the composition containing both sodium and calcium nitrate, the residues contained unreacted calcium nitrate in the acetone extract, unreacted sodium nitrate and the reaction product nitrite in the aqueous extract, and insoluble unreacted aluminum. The calcium nitrate and aluminum were the major indicators of this type of explosive and served to distinguish the residue from dynamite. Calcium carbonate was recovered in the insoluble residue in one explosion, but environmental contamination precluded positive identification of calcium carbonate as a reaction product (Appendix "B", nos. 18 and 19).

The residues from the explosives with little or no sodium nitrate provided interesting results. In one test in a room which resulted in extensive building product contamination (ceiling collapse), residue containing ammonium nitrate and aluminum was recovered from the crater. No other components or reaction products were identified, in part because of the wide distribution of calcium-containing building products. This was the only test in which any ammonium nitrate was recovered (Appendix "B", no. 21). A second test, in which residues were collected on steel, yielded a trace of unreacted nitrate (spot test only) by solvent extraction. The bulk of the residue was an insoluble white solid reaction product and unreacted aluminum. The white solid consisted primarily of calcium and aluminum, and the precise formulation has yet to be determined (Appendix "B" no. 22).

No such reaction product has previously been recovered from dynamite or "water-gel" high explosives. This test underlines that reaction products from explosives are not necessarily water soluble and re-emphasises the need for systematic analysis of residues using a variety of techniques both for recovery and for identification.

## SUMMARY

The reaction products and unreacted components from burning of "home-made" explosive chemical mixtures and from explosion of commercial "water-gel" high explosives have been identified and discussed. The scheme used for systematic analysis has given satisfactory results for residues from these types of explosives.



## APPENDIX "A"

### (a) Perchlorates and Chlorates

MIXTURE (Weight ratio)	RESIDUE	
	(UNCONFINED BURNING)	(CONFINED BURNING)
1. $\text{KClO}_4/\text{Al}$ (2:1)	$\text{KClO}_4, \text{Al}$ $\text{KCl}, \text{ClO}_3^-, \text{Al}_2\text{O}_3$	$\text{KClO}_4, \text{Al}$ $\text{KCl}, \text{ClO}_3^-$
2. $\text{KClO}_4/\text{sucrose}$ (3:1)	$\text{KClO}_4, \text{sucrose}$ $\text{KCl}, \text{ClO}_3^-$ glucose, fructose	$\text{KClO}_4, \text{sucrose}$ $\text{KCl}, \text{ClO}_3^-$
3. $\text{KClO}_3/\text{sucrose}$ (1:1) and (3:1)	$\text{KClO}_3$ $\text{KCl}, \text{CO}_3^{2-}/\text{HCO}_3^- *$	not tested
4. $\text{NaClO}_3/\text{sucrose}$ (3:1)	$\text{NaClO}_3$ $\text{NaCl}, \text{CO}_3^{2-}/\text{HCO}_3^- *$	sucrose $\text{NaCl}$
5. $\text{KClO}_3/\text{S}$ (2.5:1)	$\text{KClO}_3, \text{S}$ $\text{KCl}, \text{K}_2\text{SO}_4$	$\text{KClO}_3$ $\text{KCl}, \text{K}_2\text{SO}_4$
6. $\text{KClO}_3/\text{Al}$ (2:1)	$\text{KClO}_3, \text{Al}$ $\text{KCl}$	$\text{KClO}_3, \text{Al}$ $\text{KCl}$

\* Effervescence with dilute acid.

#### Analysis of Residues from Perchlorates and Chlorates

## APPENDIX "A"

### (b) Nitrates

MIXTURE (Weight ratio)	RESIDUE	
	(UNCONFINED BURNING)	(CONFINED BURNING)
7. $\text{KNO}_3/\text{sucrose}$ (1:1)	$\text{KHCO}_3, \text{KNO}_2$	not tested
8. $\text{KNO}_3/\text{sucrose}$ (1:1)	$\text{K}_2\text{CO}_3, 1.5 \text{H}_2\text{O}$ $\text{NO}_3^-, \text{NO}_2^-$	sucrose $\text{NO}_2^-, \text{CO}_3^{2-}/\text{HCO}_3^- *$
9. $\text{Ca}(\text{NO}_3)_2/\text{Al}$ (1.5:1)	no reaction	no reaction
10. $\text{KNO}_3/\text{S/C}$ (commercial)	$\text{KNO}_3$ $\text{K}_2\text{SO}_4, \text{KNO}_2$	$\text{NO}_3^-$ $\text{K}_2\text{SO}_4, \text{NO}_2^-$
11. $\text{NaNO}_3/\text{S/C}$ (7.5:1.5:1.0)	(i) $\text{NaNO}_3, \text{CO}_3^{2-}$ $\text{Na}_2\text{SO}_4, \text{NaNO}_2$ (residue recovered by scraping) (ii) $\text{NaNO}_3, \text{NaNO}_2$ $(\text{Na}_2\text{CO}_3)_N(\text{Na}_2\text{SO}_4)_{(1-N)} (N = 0.2 \text{ to } 0.5)$ (residue recovered by aqueous extraction)	not tested

\* Effervescence with dilute acid

#### Analysis of Residues from Nitrates

## APPENDIX "B"

Explosive	Residue-bearing surface	Components Identified
12. Tovex 5000 SD	unreacted explosive	MMAN, $\text{NH}_4\text{NO}_3$ , $\text{NaNO}_3$ , Al
13. Tovex 5000 SD	metal	MMAN, $\text{NO}_2^-$ , $\text{NaNO}_3$ , Al
14. Tovex 5000 SD	paper, wood	MMAN, $\text{NH}_4^+$ , $\text{NO}_2^-$ , Na, Al $\text{CO}_3^{2-}/\text{HCO}_3^- *$
15. Tovex 5000 SD	rags, wood	$\text{NaNO}_3$ , Al
16. Tovex 5000 SD	metal, wood	Na, Al, $\text{CO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{NO}_2^-$
17. Powermex 500	unreacted explosive	EGMN, $\text{Ca}(\text{NO}_3)_2$ , $\text{NH}_4\text{NO}_3$ , $\text{NaNO}_3$ , Al
18. Powermex 500	rags, wood	Ca, $\text{NO}_2^-$ , Na, $\text{NO}_3^-$ , $\text{CO}_3^{2-}$ , Al
19. Powermex 500	wood, metal, sand	Ca, $\text{NO}_3^-$ , Na, $\text{CO}_3^{2-}$ , $\text{NO}_2^-$ , Al, $\text{CaCO}_3$
20. Powermex 500	unreacted	EGMN, $\text{Ca}(\text{NO}_3)_2$ , $\text{NH}_4\text{NO}_3$ , Al
21. Powermex 500	wood, building products	$\text{NH}_4^+$ , $\text{NO}_3^-$ , $\text{CO}_3^{2-}/\text{HCO}_3^- *$ , Al
22. Powermex 500	metal	$\text{NO}_3^-$ , Ca, Al

\* Effervescence with dilute acid

#### Analysis of Residues from "Water-Gel" Explosives

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## IDENTIFICATION AND TRACING OF NON-EXPLOSIVE COMPONENTS IN EXPLOSIONS

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**ABSTRACT.** Non explosive components retrieved from bomb scenes frequently can be of value in determining the type of explosive device used. Additionally information may be gained to characterize these components for tracing possible origins. Methods of analysis for these components are those frequently utilized in forensic laboratories. Examples given will include microscopic examinations, X-ray fluorescence, infrared and pyrolysis G.C.

Non-explosive components retrieved from bomb scenes frequently can be of value in determining the type of explosive device used. Additionally, information may be gained to characterize these components for tracing possible origins.

Methods of analysis for these components are those frequently utilized in forensic science laboratories. Primarily (1) morphological examination, macro and microscopically, (2) inorganic analysis, X-ray fluorescence, AA, etc., (3) organic analysis, infrared spectrophotometry and pyrolysis gas chromatography.

Explosives frequently tax the investigative agencies and frustrate the law enforcement community. Records indicate that little was gained from post explosion debris in the past to warrant successful prosecution of the guilty parties. It is this reason that bombings have been used as a method of choice. In the past several years, St. Louis has had a rash of auto bombings as evidenced by nineteen injuries from auto blasts since 1970, eleven of which were fatal. Through the concerted effort of the local, state and federal government agencies we are beginning to see a phoenix rising from the ashes. Evidence of this can be seen in the successful prosecution in 1981 of a local dentist in a murder for profit scheme of the bombing death of a dental assistant and the conspiracy conviction of one in 1982 for a revenge bomb maiming of an alleged underworld enforcer. The later victim presently awaits trial for the 1980 bombing death of a reputed head of a Syrian faction. Investigations also lead to a plea of three life sentences in the bombing death of a teenager and his mother from

a device sent through United Parcel.

We have concentrated our resources in the past on the questions: What was the explosive? How big was it? etc. Why not ask first, Where did it come from? What type of package was it in? How did they place it? What makes the components unique?

Items frequently recovered consist of blasting cap leg wires, batteries, clock parts, tape, wood, paper, alligator clips, etc. These are articles used to contain or initiate the explosion and pieces of them usually survive the blast. Leg wires appear as single stranded copper or nickel wire, 18-22 gauge and plastic coated. The plastic is color coded and tables exist for looking up the manufacturer. Plastic coated copper wire, having the appearance of leg wire but with a multi-stranded core, is used as antenna wire for radio controlled devices. These devices, readily available through hobby shops, are gaining in popularity for triggering explosives. The antenna wires are color coded from one manufacturer (Leisure Dynamics) to indicate the frequency of operation, i.e. purple receives on 72.320 MHz. Hobby shops should not be over-looked when attempting to locate the origins of components and occasional visits will keep the investigator up to date on many items. The ability to recognize items in an isolated or mangled condition is quite beneficial as shown in these two examples:

### CASE 1

While processing the scene of a house bombing with two fatalities, an ATF agent immediately rec-

ognized a small metallic disc about the size of a quarter as being a glow plug used in model airplanes. It had been used as the ignition source in a pipe bomb. The glow plug, manufactured by Cox, was a high performance .049". Current was supplied with two 1.5 volt hobby batteries and casings to these were recovered. Pieces of a cardboard box remained with lettering from International Shoe Co. Checking a code number on the cardboard with the company, revealed that it was a discontinued size and no longer available. A shipping label could be pieced together that had typewriting on it. Pieces of green colored perforated pipe strap were found in the debris. An examination of the pipe strap revealed that the edges of the perforations were not green, therefore the perforations were stamped out of green stock and the color was not a product of the bombmaker. This strap material was traced to a local manufacturer, Western Wire, that made it from scraps of the manufacturing of green galvanized trash cans. The pipe strap was sold exclusively to Central Hardware stores at the time.

After several months, a suspect was developed who worked at a TV repair shop. Present in the shop was several of the discontinued cardboard boxes with the International Shoe logo. Upon further questioning, the suspect confessed and described how he built the bomb. The tripping mechanism was a toggle switch from a TV. Monofilament fishing line from the toggle to the box top flap caused the switch to throw when the lid was lifted. Two glow plugs were placed equidistant from the ends, inside of a 2"x12" pipe, filled with smokeless gunpowder. A small plastic bag of black gunpowder surrounded each glow plug.

## CASE 2

A dental assistant was killed when a bomb placed under the driver's side nearly cut the car in half. A bomb scene investigator recognized fragments of wood and metal taped together as closely resembling a pressure sensitive triggering device. The previous device was found outside the victim's garage eight months prior. It appeared in this earlier attempt that the bomb partially detonated while trying to gain entry to the garage. The dynamite evidently was defective and was scattered around the yard. Investigations and court authorized wiretaps developed sufficient information to implicate a suspect with the earlier attempt. It became important to show a similarity between

the two devices.

After receiving all of the pieces from the fatal bombing that appeared to be part of the switch, our laboratory began reconstruction of the device. Even though no common parts were used in the two triggering systems their construction was surprisingly similar. Both devices were made of black dyed balsa wood, wrapped on the ends with black electrical tape. Copper appliance wire soldered to brass strips made contact when the auto tire rolled over the trigger.

Besides the similarities in physical appearance, the following laboratory results were shown. In an attempt to reproduce the black color, balsa wood was treated with Magic Marker, Kiwi shoe polish and Higgings India Ink. Organic solubilities eliminated the Magic Marker. X-ray fluorescence of the samples showed a trace of mercury in both of the triggering devices and in the sample of Kiwi shoe polish. The Kiwi Co. eventually disclosed that their company does add mercury to their formulations as a fungicide. We did not identify the black dye on the devices but they both had the same ratio of mercury levels as that found in the shoe polish.

A microscopic examination of the solder revealed that it had been melted with something hot enough to melt the ends of the multi-stranded copper wire, probably a torch. An elemental profile was performed by bulk mode X-ray Fluorescence (XRF). In an attempt to select peaks of close intensity for ratioing the Tin  $K_{\alpha}$  and the Pb  $L_{\alpha}$  were selected. Analysis of both devices revealed a tin content of 50% in each.

The comparison revealed that even though the parts had a different origin the technology and the expertise in the design and construction of the two triggering devices was the same. This information was used in the successful prosecution of a local dentist in what turned out to be a murder for profit scheme.

## CONCLUSION

This is only two examples where non-explosive components retrieved from the blast site helped to understand the mechanism of the device and to bring these cases to a successful conclusion. A concerted effort must be made to gain as much information as possible out of the device parts. A well trained trace evidence analyst, working with the explosive residue analyst, is a great complement.

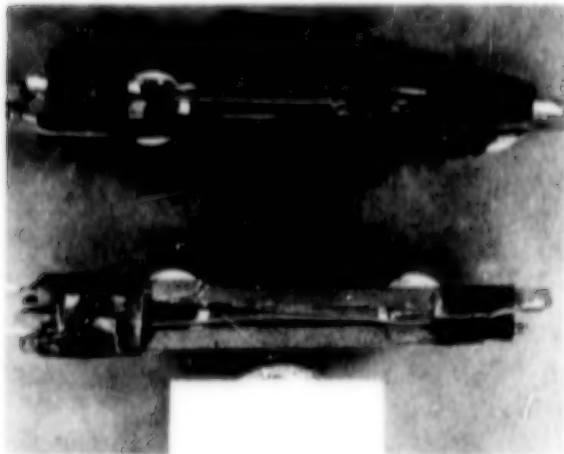


Figure 1. Comparison of triggering device from bombing attempt (top) and reconstructed device from fatal blast (bottom).



Figure 2. Solder examination of fatal blast (top) and attempt (bottom).

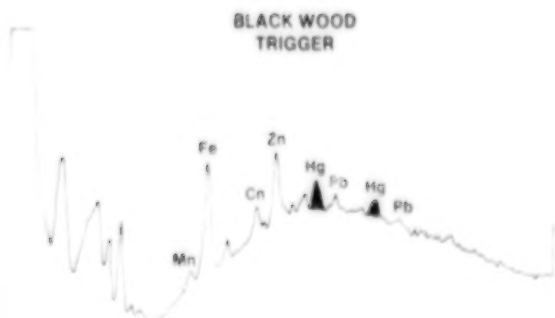


Figure 3. X-ray fluorescence (XRF) of black dyed wood trigger showing traces of mercury.

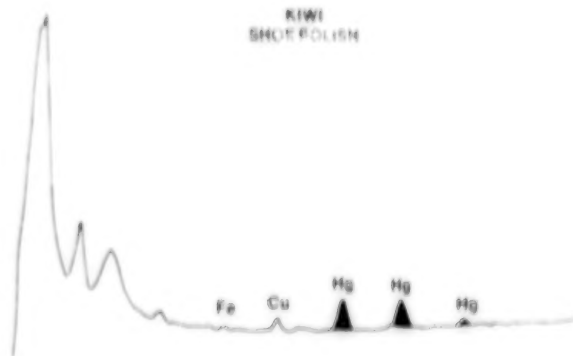


Figure 4. XRF of Kiwi shoe polish. Mercury added as a fungicide.

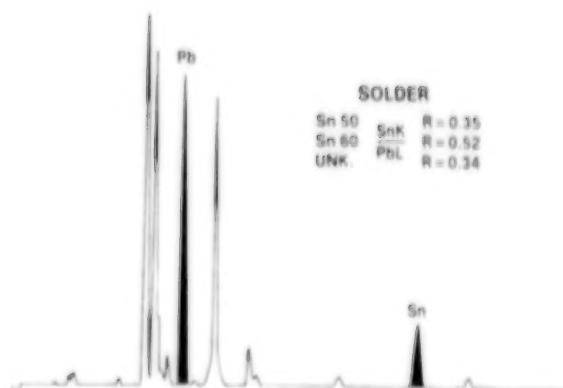


Figure 5. XRF of Solder on trigger device. S K : pb L ratio is 0.34.



Figure 6. Glow plug used in model airplanes found at scene of blast fatal to two. This was the source of ignition in a pipe bomb. Note size in comparison to screw.



Figure 7. Debris found in house blast fatal to two. Items that can be seen are (1) 1.5 volt hobby batteries, (2) green pipe strap (3) cardboard box.

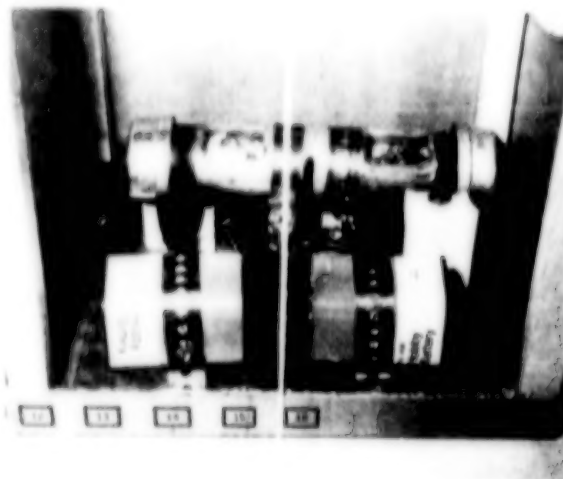


Figure 8. Reconstructed bomb sent through the United Parcel Service.



## EXPLOSIVE ANALYSIS KIT

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**ABSTRACT.** An explosive analysis kit was developed to perform the timely field separation and identification of 28 different explosives and energetic materials. The kit uses solubility and thin-layer chromatography (TLC) to separate mixed explosives and identify each explosive component. The kit, with sufficient materials to perform ten analyses, is packaged in a briefcase. The solvents for sample dissolution and TLC separation are packaged in single-use lead tubes to insure composition and lack of contamination. The kit is assembled from commercial components, with custom packaging required for filling and sealing the lead solvent tubes. A battery-operated ultraviolet (UV) light visualizes the TLC plates, eliminating the need for corrosive reagents and ambiguous color-forming reactions. A worksheet, provided with the instructions, guides the operator through the analysis and is used to record data and help make the identification. The kit identifies the components of booster and main charge explosives, as well as selected oxidizers, propellants, and other energetic materials. After limited training, 62 U.S. Marine Corps EOD technicians tested the kit. Their performance was good, and their reaction to the kit was very favorable.

### INTRODUCTION

The Naval Explosive Ordnance Disposal Technology Center (NAVEODTECHCEN) is responsible for the research and development of specialized equipment, techniques, and procedures required to support operational explosive ordnance disposal (EOD) units in the location, neutralization, and disposal of surface and underwater explosive ordnance. This Joint-Service program encompasses all current and obsolete explosive ordnance (both domestic and foreign), including improvised explosive and nuclear devices that may be

employed by dissident and terrorist groups. NAVEODTECHCEN also provides significant support to activities concerned with the demilitarization of chemical weapons and the reclamation of ordnance-contaminated land and water areas. Finally, support is provided to the Federal Bureau of Investigation, the Secret Service, civilian law enforcement agencies, and other government departments.

In response to a Marine Corps requirement, an explosive analysis kit was developed to allow EOD technicians to identify in the field 28 explosives and energetic materials (see Table 1).

Table 1. LIST OF EXPLOSIVES AND ENERGETIC MATERIALS

Common explosives	Special purpose explosives	Energetic plasticizers	Pyrotechnic ingredients
TNT	TNB	FEFO	Potassium
Nitroglycerin	DATB	TEGDN	chlorate
Tetryl	DIPAM	2,4 DNT	Barium nitrite
RDX	HNS	MTN	Ammonium
HMX	TATB	BDNPA	perchlorate
HND	R-salt	BDNPF	
PETN	BTNEU		
Ammonium picrate	BTNEN		
Picric acid			
Nitrocellulose			
Ammonium nitrate			

This kit was developed at the Naval Surface Weapons Center, White Oak, Maryland, where scientists were given a list of explosives to be identified and general guidelines. The analysis system they recommended employed both solubility measurement and thin-layer chromatography (TLC) to identify the explosives (see NSWC TR 79-455). The kit consists of a carrying case, reusable components, and enough single-use components for ten analyses. Currently packaged in a briefcase, the kit weighs 5.9 kilograms (13.0 pounds) and occupies 0.014 cubic meter (0.5 cubic foot) of space. The cost of a prototype kit capable of performing ten analyses is estimated to be \$1,000, with approximately half that cost for reusable components. It is anticipated that refills for the single-use components will be fielded as a ten pack containing all single-use components, plus low-cost multiuse components and analysis worksheets.

Operational suitability of the kit was demonstrated using the personnel of the EOD units at Twenty Nine Palms and Camp Pendleton, California, and at Beaufort Air Station, South Carolina, and Camp Lejeune, North Carolina. The personnel were trained, divided into teams, and allowed to proceed at their own pace. The teams were given unknown explosives, serialized worksheets, and a questionnaire to be completed after the evaluation.

### DESCRIPTION

The reagents to perform the solubility measurement and TLC tests are packaged in single-use tubes. The solvents for the TLC separation are mixed with about 6-percent Cab-O-Sil, a finely divided silica, to form a gel the consistency of toothpaste. This gel allows the solvent to be handled as a solid. Fielding single-use tubes insures the user that the proper solvent mixtures are instantly available. The tubes are color coded red, white, and blue for identification. Upper storage and use temperature has been set at 50°C (122°F) because the boiling point of acetone, which is used for explosive dissolution, is 56°C (133°F).

Three simultaneous TLC separations are performed using three different hexane ethyl acetate solvent mixtures. In thin layer chromatography, a solvent or mixture of solvents proceeds by capillary action up a plate covered with a thin layer of silica gel or other high-surface-active area materials. The material to be separated is not only carried along with the solvent but is also absorbed by

the silica gel. The time a component spends in the solvent versus the time it spends in the gel determines how far up the plate it travels. The relative distance the sample travels is expressed as a ratio of the distance the sample travels divided by the distance the solvent travels. The ratio, commonly called the RF value, should ideally be constant; however, it is affected by changes in solvent composition, the degree of sample loading, the activity of the TLC plate, etc. For this reason, a reference sample mixture has been included in the explosive analysis kit. The reference sample is a mixture of the explosives TNT, picric acid, RDX, and tetryl. The quantity contained, about 16 milligrams per sample, is small enough to be exempt from Navy Explosive Safety Stowage and DOT Hazardous Materials regulations.

The silica gel on the TLC plate contains dye which fluoresces orange when excited with short-wave-length (254 nm) ultraviolet (UV) light. A majority of explosives absorb strongly in this region of the spectrum and show up as dark spots on an orange background when the TLC plate is interrogated with the UV light.

### USE OF THE KIT

The analysis of an unknown explosive or mixture of explosives can be broken into four major steps: preparation, separation, visualization, and identification. The use of the kit will be illustrated by a typical analysis.

A spatula and allen-head bolt are used to measure about 100 milligrams of explosive into each of two vials. One milliliter of water is added to one vial, and 1 milliliter of acetone is added from a lead tube to the other vial. One milliliter of acetone is also added to the reference sample. The samples are allowed to dissolve. The extent of solution and appearance is noted on the worksheet.

Using disposable 1-microliter pipettes, 1-microliter spots of each solution are placed on each of three 2-by-7 centimeter TLC plates. The plates are placed in plastic developing chambers charged with solvent gel of three hexane ethyl acetate mixtures. The mixtures' compositions (6:1, 3:1, and 1:3) provide a range of polarity capable of separating the explosives of interest. About 5 minutes is required for the solvent to proceed up each TLC plate, then the plates are removed, labeled, and allowed to dry.

Each TLC plate is viewed or visualized by the UV light. The silica gel fluoresces orange, but the UV light is absorbed by the explosives, resulting in

a gray, nonfluorescing spot on the plate. The position of the separated explosives is marked on the plates and the distance the explosive traveled relative to the solvent is calculated. The reference sample has been included to increase the analyst's confidence in the procedure as well as show where the frequently encountered explosives, TNT, tetryl, RDX, and picric acid, are encountered.

Identification of the unknown is based on all information available to the analyst: RF value, explosive and photo-oxidation color, solubility, and origin. Identification by this field system is not unequivocal; similar explosives (i.e., RDX and HMX) may differ only slightly; therefore, all clues must be used. Mixed explosives will produce several spots on the TLC plate—one from each explosive. Aluminized explosives will be indicated by a gray, undissolved residue.

### OPERATIONAL TESTS

Operational tests were conducted using Marine Corps EOD technicians to determine if the kit could be reliably operated, to identify any resolvable shortfalls in the kit, and to determine the appropriate training and practice levels. The testing was conducted in two series, preliminary tests in the spring of 1980 in California, followed by additional tests in the spring of 1981 in North and South Carolina. Between these two series of tests, the instructions were modified to correct deficiencies revealed, and the rechargeable battery-operated UV light was replaced by a larger lan-

tern-battery-powered unit.

A total of 62 technicians working in teams used the kit to perform analyses on 87 unknowns. During the testing, 20 different unknowns were used, five of which contained two different major ingredients, for example, pentolite which contains TNT and PETN. Of the analyses, 72 percent were totally correct. The incorrect analyses tended to be one explosive identified as a similar explosive. The conclusion reached was that the options facing the analyst were too great. In the kit planned for fielding, most or all of the energetic plasticizers and special-purpose explosives will be dropped, reducing the identification options available to the operator.

### CONCLUSIONS

Results of the testing demonstrate that the explosive analysis kit allows the field identification of various explosives and energetic ingredients by nonscientific personnel.

The Marine Corps EOD technicians evaluating the kit reacted very favorably and achieved a correct analysis rate of 72 percent.

Deficiencies of the kit that resulted in false identification or missed components have been identified. Proposed corrective actions include: reducing the number of options by eliminating those explosives not frequently encountered, providing more extensive training to the personnel before the actual performance of the test, and cataloging explosives by their usual application.

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## ORGANIC SOLVENT EXTRACTS OF EXPLOSIVE DEBRIS: CLEAN-UP PROCEDURES USING BONDED PHASE SORBENTS

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**ABSTRACT.** A number of sensitive techniques exist today for the detection of explosives. However all their sensitivity and specificity may be lost when "dirty" or "real world" samples are subjected to analysis. Improved chromatographic techniques and sensitive detectors have aided the situation. Unfortunately, many of the "real world" samples encountered contain a complex mixture of interfering substances. The chromatography systems can not adequately separate the explosives of interest from these contaminants. These "dirty" samples require a pre-treatment prior to being subjected to chromatography and detection. The use of porous polymers and bonded phase adsorbents as a clean-up procedure is explored in this work. Retention properties of both explosives and contaminants are studied, and an analytical scheme is presented which optimizes the separation of the explosive from the contaminants.

### INTRODUCTION

The identification of high explosives (TNT, RDX, Tetryl and PETN) in post-blast debris usually involves extracting the debris with a suitable solvent such as acetone or methanol and analyzing the extract by chromatography coupled with a detection technique. Many of the techniques, such as Thin Layer Chromatography (TLC), High Performance Liquid Chromatography/Mass Spectroscopy (HPLC/MS), Gas Chromatography/Mass Spectroscopy (GC/MS) or HPLC/UV allow detection at the nanogram and picogram levels. However, contaminants extracted from the debris with the explosive of interest often make these sensitive detection techniques useless.

Many times "dirty" samples contain greater quantities of contaminants than they do explosives. The sample to be analyzed is, therefore, often composed of a small amount of explosive in a large quantity of a complex, dirty matrix. Experience has shown that chromatographic techniques (TLC, HPLC and GC) alone are not sufficient to separate the explosive from the contaminants, and provide clean samples to the detectors. As a result, detectors often respond to the contaminants, masking the detection of the explosive of interest.

This contamination problem initiated work on clean-up procedures.

Our initial work examined the use of Rohm and Haas AMBERLITE XAD resins to clean up explosive residue extracts. We found that XAD-2 (cross-linked styrene divinylbenzene porous polymer) and XAD-7 (porous polymer with an alkyl ester functional group) resins retained and eluted explosives from various aqueous solvent systems with high recovery rates. Unfortunately they also retained and eluted many of the contaminants in the sample matrix. In an effort to attain a greater selectivity a series of bonded phase sorbents was examined.

### MATERIALS

The sorbents were obtained from Analytichem International, and are known as their BOND ELUT (TM) system. The system consists of columns which are available with 18 different bonded phases. The column packing is silica gel which has a monofunctional chemical moiety attached. Those phases evaluated are shown in Table 1. The bonded phases tested were selected because their functional groups were expected to be effective in selectively retaining explosives from various solutions.



**Table 1. BONDED PHASES TESTED FOR RETENTION OF EXPLOSIVES**

Bonded Phases Tested			
Analytichem Bond Elut (TM) Columns			
Column volume: 2.8 ml			
Sorbent mass: 500 mg.			
Non-Polar		Polar	
C18	Octadecyl	CN	Cyanopropyl
C8	Octyl	20H	Diol
C2	Ethyl		
PH	Phenyl		
CH	Cyclohexyl		

In theory, a high degree of selectivity toward the explosive should be possible by taking advantage of the interaction of the isolate (explosive) with the bonded phases and the solvents used (which change when extracting debris, depositing the sample on the column or eluting the isolates).

A standard explosive mixture (SEM) which included RDX, TNT, Tetryl, and PETN at 10 PPM concentrations in acetone was used throughout the study. The samples were placed on the columns by aspirating the sample, in a suitable solvent, through the column. Samples were eluted with two 500  $\mu$ l washes of solvent placed on the top of the column. The column was then centrifuged with the sample and eluent passing into a suitable receiver (13 x 100 mm culture tubes). Columns were conditioned prior to use according to manufacturer's instructions.

A Waters Model 6000A HPLC pump using a Radial-PAK C-18 column with the Radial Compression Module and Waters Model 441 UV detector set at 214 nm was used to measure quantities of explosives recovered. The mobile phase was acetonitrile:water 70:30 run isocratically with a 1.0 ml/minute flow rate.

#### **COLUMN EVALUATION—RETENTION OF EXPLOSIVES**

The first step in evaluating each bonded phase was to measure its effectiveness in retaining and subsequently eluting the explosives. The non-polar phases were examined first. These phases function by retaining hydrophobic organic compounds from reverse phase solvent systems. Since explosives are separated from debris using polar solvents (*e.g.* acetone or methanol) it was necessary to convert the solvent containing the explosive to an aqueous system in order to promote retention of the explosive on the column. A 10 fold volume of deionized water was added to the SEM. This 1 ml acetone/10 ml water solution containing 10  $\mu$ g of each explosive was then passed through the non-polar column with vacuum.

The columns were then eluted with 0.5 ml of 70:30 acetonitrile:water and analyzed by HPCL/UV using peak areas to determine the quantity of explosive retained and recovered.

Of the columns evaluated only the CH, C18 and PH bonded phases showed good retention (better than 95% recoveries) from the acetone/water.

The polar columns, CN and DIOL, which were also reported to retain materials from the reverse phase were similarly evaluated. Testing showed that they were not effective in retaining explosives from acetone/water mixtures.

Although the polar columns were not effective in a reverse phase system their use with a non-polar solvent system needed to be evaluated. Methylene chloride ( $\text{CH}_2\text{CL}_2$ ) was chosen as a solvent since the explosives of interest are soluble in it. A 10 PPM mixture of the same explosives in  $\text{CH}_2\text{CL}_2$  was prepared. Hexane was added to the  $\text{CH}_2\text{CL}_2$  explosive mixture (1:1) to make the system more non-polar and to promote the retention of the explosives on the polar CN and DIOL columns. The explosives were then eluted with 0.5 ml of 70:30 acetonitrile:water and analyzed by HPLC/UV, as was done previously. The CN column proved to be more efficient than the DIOL column in the recovery of TNT and PETN. Recoveries for the other explosives were approximately equal (95% recoveries or better) on both columns.

#### **RESULTS AND DISCUSSION**

The results of the column evaluation are summarized in Table 2. These results led to the establishment of the analysis scheme in Figures 1 and 2. Samples are first placed on the column in a solvent (acetone) to which 10 parts of water have been added. Once the explosives have been retained, the columns can be washed with a 20:80 acetonitrile:water mixture (2 column volumes) to remove polar contaminants. The CH column was chosen because of high recoveries and its superior selectivity compared to the C18 column. The CH col-



**Table 2. COLUMN EVALUATION STUDY. SUMMARY OF RESULTS.**

Columns	Explosives Extracted	Eluting Solvents	Cleaning Solvents*	Contaminant Removed
C18,CH,PH	From aqueous system A	70:30 CH <sub>3</sub> CN:H <sub>2</sub> O or 1:1 CH <sub>2</sub> Cl <sub>2</sub> :Hexane	20:80 CH <sub>3</sub> CN:H <sub>2</sub> O	Polar
CN	From non-polar	70:30 CH <sub>3</sub> CN:H <sub>2</sub> O	Hexane	Non-polar
C2:C8	NOT EFFICIENT IN RETAINING EXPLOSIVES FROM SYSTEM A			
DIOL	NOT EFFICIENT IN RETAINING TNT, PETN FROM SYSTEM B			
<b>SYSTEM</b>				
A	10:1 H <sub>2</sub> O:ACETONE—Polar System			
B	1:1 CH <sub>2</sub> Cl <sub>2</sub> :HEXANE—Non-Polar System			

\*Solvent which could be used to rinse the column containing the explosives without eluting the explosives. These are only two of numerous solvents, or solvent combinations, which need to be examined.

umn is then placed on the CN column by means of an adaptor and the explosive is eluted using a mixture of methylene chloride:hexane 1:1. As seen from previous column evaluation, the explosive will now be retained on the polar CN column. Column afterwash studies had shown that the CH<sub>2</sub>CL<sub>2</sub>:hexane completely eluted the explosives from the CH column with two 0.5 ml washes. The CN column can now be washed with hexane to remove non-polar contaminants (two column volumes). The final elution of the explosive from the column is accomplished using the HPLC mobile phase (acetonitrile:water 70:30). The mobile phase (0.5 ml) is placed on the column and centrifuged through the column into a suitable container (13 x 100 mm culture tube). The sample is then ready for HPLC analysis. Results of recovery studies using

this procedures for the SEM is shown in Table 3.

**TABLE 3. Recovery study results for various explosives.**

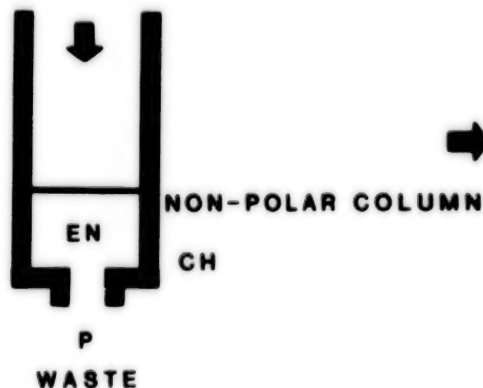
10 PPM of the SEM was placed on the CH column from an acetone:H<sub>2</sub>O solution. The column was then eluted with CH<sub>2</sub>CL<sub>2</sub>:hexane (1:1) onto a CN column. The explosives were eluted with the HPLC mobile phase.

Explosive	Percent Recovery
HMX	24% <sup>a</sup>
RDX	99%
TNT	94%
Tetryl	96%
PETN	95%

a. The poor recovery for HMX was a result of attempts to optimize the cleanup procedure for the five commonly encountered explosives. HMX can be recovered with greater efficiency by changing various procedural parameters.

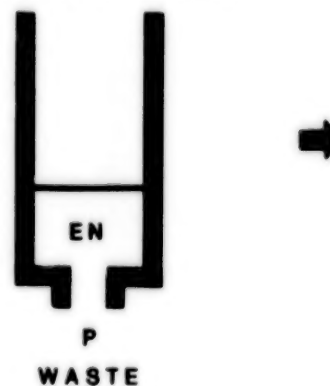
#### SAMPLE ON COLUMN

ACETONE/H<sub>2</sub>O 1:10



#### WASH

CH<sub>3</sub>CN/H<sub>2</sub>O 20:80



E - EXPLOSIVES  
P - POLAR CONTAMINANTS  
N - NON-POLAR CONTAMINANTS

Figure 1. (A) Explosives are extracted from the acetone/H<sub>2</sub>O solution and trapped on the CH column. (B) Cleansing solvents can then be used to further remove polar contaminants.

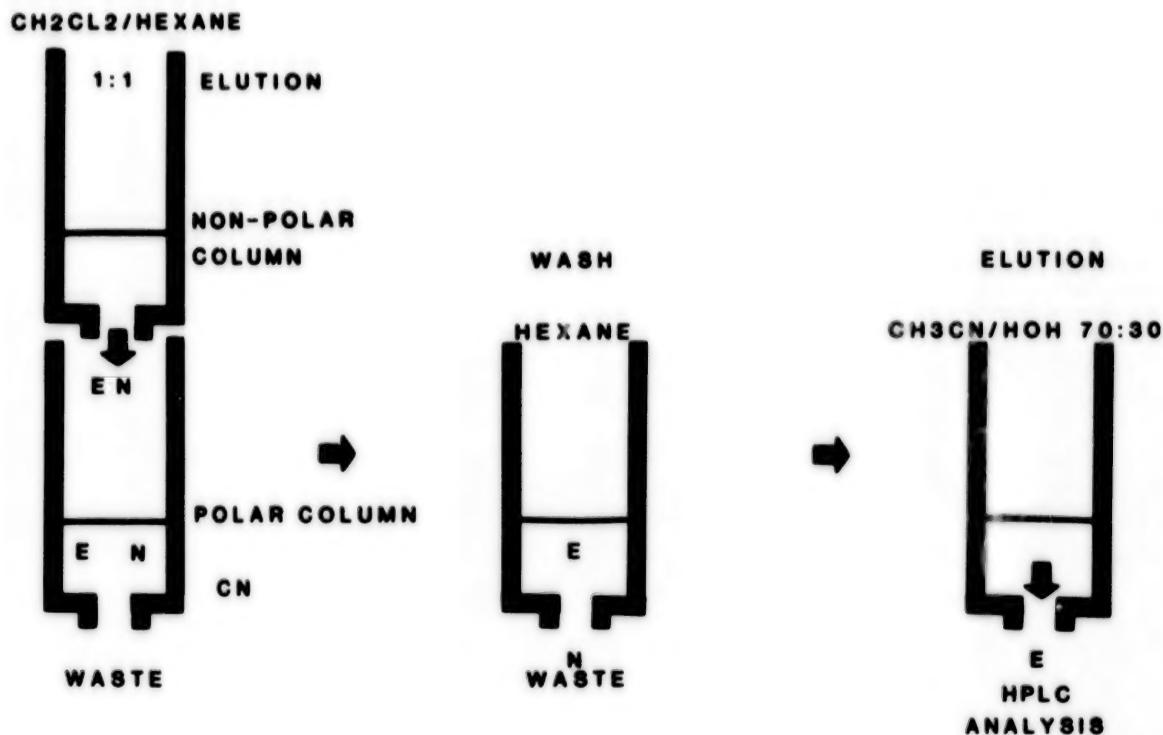


Figure 2. (C) The explosives are eluted from the CH column and trapped on the CN column. (D) The CN column can then be washed with cleansing solvents. (E) Explosives are then eluted with the HPLC mobile phase for analysis.

This procedure makes use of the dual character of the explosives examined which may allow interfering materials extracted with them to be removed prior to analysis. The explosive molecules have both a large non-polar hydrocarbon portion to their structure as well as a polar portion. These properties allow the molecules to be retained on a non-polar column from a polar solvent system while allowing the polar contaminants to pass through. The explosives can then be eluted with a moderately non-polar solvent system onto a polar column. As the explosives are retained on the polar column, non-polar contaminants pass through as waste.

#### Additional Sample Clean-up

After application, the explosives are attached to the bonded phase of the column. This mechanism will allow for additional clean-up of the sample prior to analysis. When bound to the non-polar phase, polar cleansing solvents should remove additional polar contaminants. When bound to a polar phase a non-polar cleansing solvent should remove additional non-polar contaminants. Table

2 lists two cleansing solvent systems that have been used with minimum loss of explosives. Due to the complexity of postblast debris, additional work with cleansing solvent systems is needed. Since blast debris varies from case to case the retention properties of the contaminants to the bonded phases also needs further study.

#### CONCLUSION

Organic explosives can be retained on bonded phase sorbents utilizing the explosive molecule's ambivalent character. Both polar and non-polar sorbents work well for retaining the explosives studied. Virtually complete recovery can be obtained through the procedure. The sorbent properties of the bonded phase columns lend themselves to pre-analysis sample clean-up.

#### ACKNOWLEDGEMENT

We wish to thank Carl Selavka, a graduate student at Northeastern University for his assistance in this work.

## A SCHEME FOR THE ANALYSIS OF EXPLOSIVES AND EXPLOSIVE RESIDUES

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**ABSTRACT.** The FBI Laboratory has developed a new scheme for the analysis of explosive residues. This scheme is based on a water and/or organic solvent wash of bombing debris. Inasmuch as several high explosives such as dynamites and water gel/slurries contain both organic and inorganic species, it is often necessary to fully identify the explosive, to perform both washes on the debris. This scheme highlights the use of x-ray powder diffraction and ion chromatography (IC) for the analysis of the water wash. Such hard to identify inorganic species as monomethylamine nitrate can easily be identified with the IC methods reported. The organic solvent wash highlights the use of HPLC and GC/MS methods. HPLC methods utilize both normal and reverse phase chromatography and variable UV wavelength and TEA detectors.

During the past 2-3 years the FBI Laboratory has been involved in the investigation of hundreds of terrorist and other criminal bombings. These bombings were committed with a wide variety of explosives, from low explosives, such as, home-made black powder to high explosives, such as, water gel/slurries or military demolition explosives like TNT or C-4.

Many of the high explosives, when undergoing a high order detonation leave little or no residue, making their detection very difficult. When the bombing is, for example, of a building, the problem of detecting the explosive is compounded because traces of residues left at the scene could be mixed with tons of building debris.

Faced with many high explosives capable of leaving only traces of residues, complicated crime scenes, and numerous requests from state and local laboratories for the FBI Laboratory's procedure for explosive analysis, the Instrumental Analysis Unit (IAU) of the FBI Laboratory developed a scheme for the analysis of explosives and explosive residues. It was felt that the development of a formal procedure or scheme utilizing the latest instrumentation was necessary to give the explosive analyst an edge when faced with some of the previously mentioned problems.

Figure 1 represents the overall scheme for explosive and explosive residue analysis developed by

the IAU of the FBI Laboratory. This scheme has been used very successfully for the past two years and has resulted in the successful analysis of hundreds of bombing cases and the identification of the explosive used.

This paper will highlight the four main instrumental methods noted in the scheme. X-ray powder diffraction (XRPD), ion chromatography (IC), liquid chromatography (HPLC), and gas chromatography/mass spectroscopy (GS/MS).

The first step in the analyses of debris from a bombing is often a head space analysis. When the debris contains soil, small concrete fragments, plaster, synthetic rubber foam, cloth fragments,

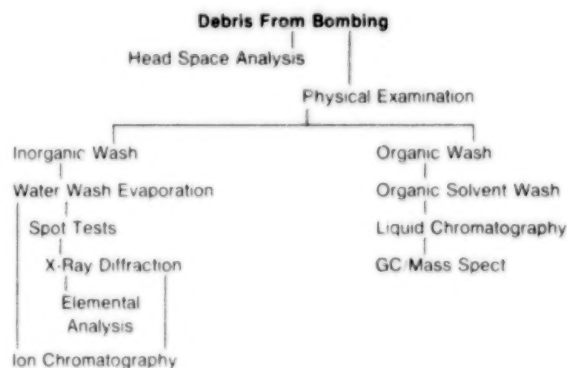


Figure 1. Scheme for the Analysis of Explosives.

or other small absorbent type material a head space analysis is conducted and any volatile organic explosive materials usually can be removed and identified.

The debris to be analyzed is placed in a one gallon aluminum paint can, gently heated on a hot plate, while the volatile vapors are removed from the top of the can by sucking them off with a vacuum. All vapors, explosive and otherwise, are trapped on a 1½-inch charcoal trap. The volatile materials are then washed off the charcoal trap with dichlorethane and analyzed by HPLC. The actual analysis will be discussed in the HPLC METHODS section.

After the head space analysis, or if the debris would physically not permit a head space analysis, such as large metal fragments from a car or plane, the next step is a physical examination of the debris. This could also include a microscopic examination of small metal fragments, such as, from a pipe bomb.

The object of the physical examination is to determine if anything foreign to the debris is present or if anything of evidentiary value can be observed. Also at this time the debris is often divided into two parts; one part to be washed with water, the other with an organic solvent, such as, acetone. An alternate approach is to first wash the debris with acetone and then water.

Although the water wash is to remove inorganic residues and explosives and virtually all low explosives are inorganic in nature; numerous high explosives, such as the dynamites, water gel/slurries and ammonium nitrate/fuel oil mixtures also contain inorganics, making the water wash necessary for a complete high explosive analysis.

The acetone wash is designed to remove the organic explosives from the debris. Most organic components found in high explosives, such as, TNT, nitroglycerin (NG) and pentaerythritol tetranitrate (PETN) are relatively soluble in acetone and will be removed in a wash.

Looking first at the water wash, it is conducted with distilled or deionized water. As small a quantity of water as possible should be used i.e., 25-50 ml of water, for typical pipe bomb fragments to 150-300 ml of water for larger metal fragments. From this initial wash a 5-10 ml aliquot is removed for the IC analysis, while the rest is evaporated to dryness.

The evaporate is used for spot tests and for XRPD analysis. Spot tests conducted routinely by the IAU are summarized in Table 1.

**Table 1. SPOT TEST FOR EXPLOSIVE RESIDUES**

Reagent	Test
1% Silver Nitrate	Chlorides
3% Barium Chloride	Sulfates
5% Diphenylamine	Oxidizing Agents (Nitrates)
Nitron	Nitrates
Potassium Hydroxide	Ammonium
Hydrochloric Acid	Carbonates
Aniline Hydrochloride	Chlorates

## **X-RAY POWDER DIFFRACTION METHODS**

XRPD is an instrumental method of analysis in which the intensity of X-rays diffracted from a crystalline specimen is recorded as a function of the diffraction angle. The diffraction angle or X-ray peak is related to the distance between crystal planes or "d" value. Individual "d" values make up the diffraction pattern for a crystalline substance.

The basis of XRPD, that makes it valuable in explosive residue analysis is it gives a chemical fingerprint of each substance analyzed. Every crystalline material gives a characteristic X-ray pattern and no two chemically distinct substances give identical patterns. It is only necessary to match the pattern of an unknown substance with a known pattern to make an identification.

### **Instrumentation**

The IAU uses Philips XRG 3000 and 3100 Generators which are equipped with a Philips vertical diffractometer, graphite monochromator and solid state scintillation counter. The X-ray generator is operated at 45 Kv and 35 mA and yields standard  $\text{CuK}_\alpha$  radiation at 1.5418 Å from the copper target X-ray tube.

Each specimen was scanned in the 2θ range from 60° to 0° at 1° per minute. The "d" values were searched through JCPDS search manuals using the Hanawalt Method.

### **Applications**

Although XRPD can be applied to explosive and explosive residue analysis in many different ways, in this work they are divided into three areas as follows: 1, Analysis of Post-Blast Explosive Residues, 2, Identification and Confirmation of Pre-Blast Explosives, and 3, Identification of Unknown Materials.

Both high and low explosives can leave enough post-blast residues to be recovered and analyzed by XRPD but the high explosives are limited to some dynamites, water gel/slurries and some ammonium nitrate mixtures. Most of the residues re-

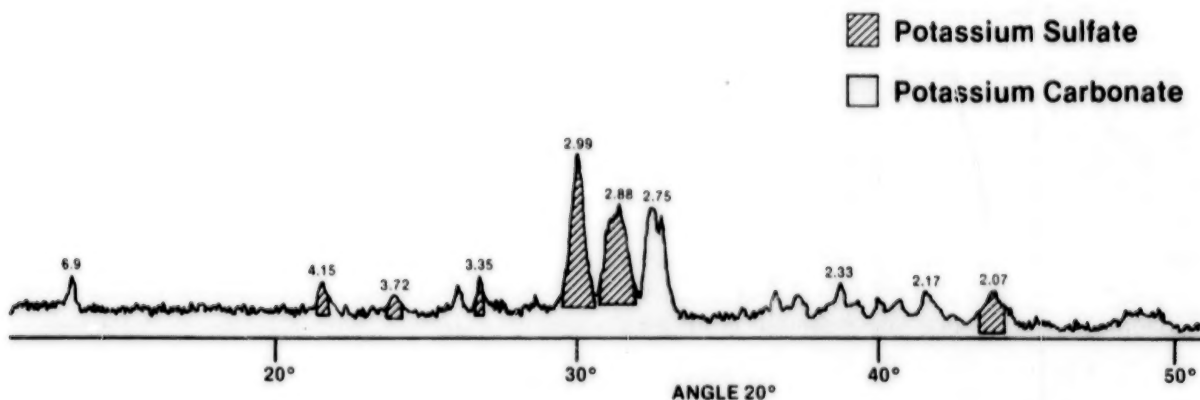


Figure 2. XRPD of Black Powder Combustion Products.

covered in sufficient amounts for analysis are low explosive combustion products.

The most common low explosive used in improvised explosive devices (IED's) today is black powder. Figure 2 shows the X-ray diffractogram of the residue from a black powder pipe bomb. Both potassium sulfate and potassium carbonate have been identified in the residue. Based on this analysis a determination could be made that black powder was the main explosive used.

XRPD is a very powerful tool in identifying solid residues in post-blast situations and can be applied, as shown in Figure II, to mixtures.

Another useful application of XRPD is to confirm the identity of a known explosive in pre-blast situations. Figure 3 shows the diffractogram of an unknown explosive taken from an IED that was found on an airplane in Brazil. A simple interpretation procedure reveals the material to be PETN. XRPD again offers a quick and easy method of

confirming the identity of materials known to be explosives.

The last application of XRPD in explosive analysis is its value to identify unknown materials *i.e.*, materials taken from searches of suspects home or business, and those found at or near the bombing scene.

#### ION CHROMATOGRAPHY METHODS

Ion Chromatography is a term coined by the Dionex Corporation to encompass all techniques used for separating and quantitating both inorganic and organic ions, and in its broadest sense is the chromatography of ions. IC combines the efficient separation capabilities of ion exchange resins with conductometric detection. Conductometric detection is an ideal technique to monitor ion exchange separations because of its universal and linear response.

Ion exchange resins used in IC are spherical in

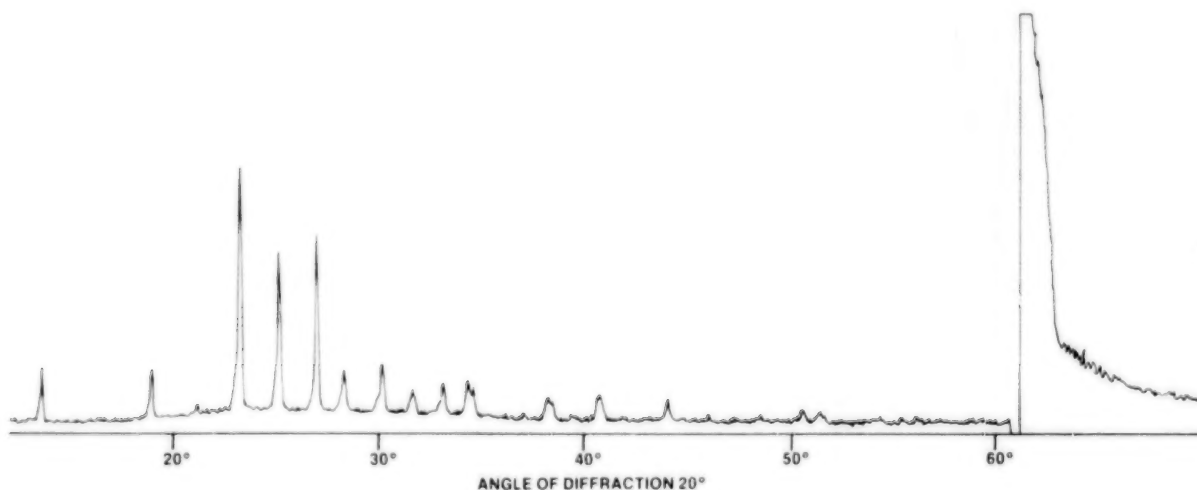


Figure 3. XRPD of PETN.



nature composed of a polystyrene matrix cross-linked with divinylbenzene. Functional groups, such as, sulfonic acid and quaternary ammonium are chemically bonded to the matrix. These groups provide exchange sites where their counter ions are exchanged with sample ions as the sample flows through the resin bed. Retention time depends on several factors, the most notable are: (1) resin characteristics, (2) ion size, (3) ionic charge, (4) ion concentration and ionic composition of the mobile phase.

#### Instrumentation

The IAU uses a Dionex Ion Chromatograph Model 16 to perform its explosive residue analysis. The Model 16 is equipped with a 100 ul sample loop and a 6 ul flow through conductivity detector. Figure 4 is a photograph of the Dionex Model 16.

Since IC is a form of liquid chromatography it has a mobile and stationary phase. The mobile phase or eluent differs according to the type of analysis being performed. In explosive residue analysis there are two basic types of analysis; anion and cation. The eluent for standard cation analysis is 0.01 N HCl in 30% methanol.

The columns used in the standard cation analysis are as follows: 3 x 50 mm Dionex pre-column and a 6 x 200 mm Dionex cation separator column

in series with a Dionex 9 x 150 mm cation suppressor column.

In standard anion analysis the eluent is 0.003M NaHCO<sub>3</sub>/0.0024M Na<sub>2</sub>CO<sub>3</sub> at a flow of approximately 3.0 ml/min. The columns are a 3 x 50 mm Dionex pre-column and a 4.0 mm x 250 mm Dionex separator column in series with a Dionex anion fiber suppressor.

Other detectors used in the analysis of explosives are a Dionex Electrochemical Detector with a 2.6 ul cell and a Perkin Elmer LC-55 variable wavelength UV-VIS. spectrophotometer equipped with a 10 ul cell. Detection is measured at 210 nm.

Figure 5 is a block diagram illustration of the IC set-up of the IAU.

Basically the operation is as follows: A mixture of sample cations containing, for example, Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> is injected into the mobile phase of .01 N HCl in 30% methanol. Sulfonic acid exchange sites in the separator column, exchanges H<sup>+</sup> for the Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions. After the ions are separated on the ion exchange bed they exit at various times from the bottom of the column in a background of HCl eluent.

The mixture then enters the second column, the suppressor, containing a strong base ion exchange resin in the OH form. Two reactions take place. First the background HCl ions of the eluent are removed leaving deionized water. The cations are converted to their hydroxides in the second reaction and their conductivity is measured now in the suppressed background of water.

#### Applications

There are basically two applications of IC to explosive analysis. They are as follows: (1) Trace analysis of post-blast explosive residues, (2) Identification of pre-blast explosive components.

By far the widest application of IC in explosive analysis has been trace analysis of post-blast residues. Table 2 summarizes some of the cation and anions that can be analyzed by IC.

Figures 6 and 7 show the separation of the normal cations and anions, respectively, as detected with the conductivity detector.

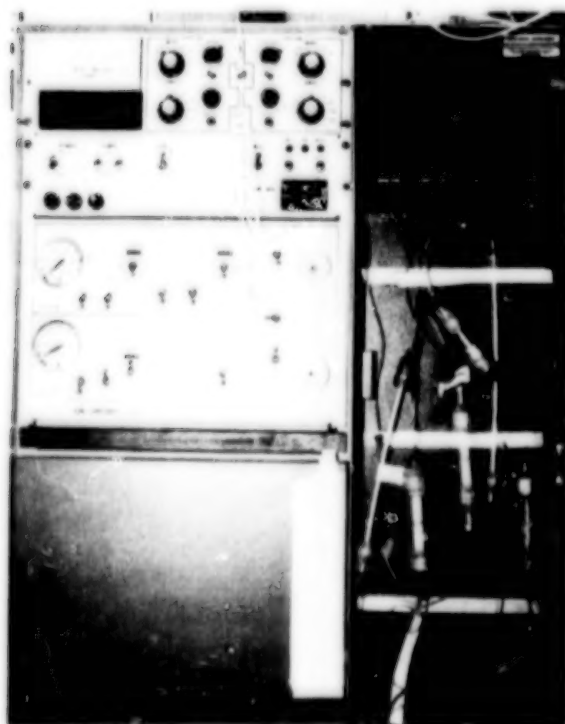


Figure 4. Photograph of an Ion Chromatograph.

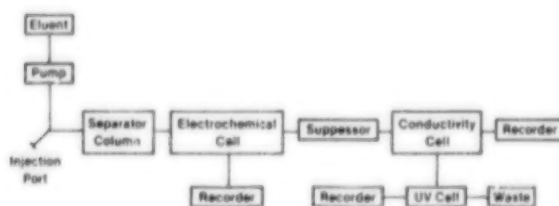


Figure 5. Block Diagram of Ion Chromatograph Set-Up.



**Table 2. IONS ANALYZED BY IC IN EXPLOSIVE RESIDUES**

<b>I Cation Analysis</b>	
monovalent $\text{Na}^+$ , $\text{K}^+$ , $\text{NH}_4^+$ , *MMA <sup>+</sup>	Detector System
divalent $\text{Ca}^{++}$ , $\text{Mg}^{++}$ , $\text{Ba}^{++}$ , $\text{Sr}^{++}$	conductivity
<b>II Anion Analysis</b>	
$\text{F}^-$ , $\text{Cl}^-$ , $\text{NO}_2^-$ , $\text{Br}^-$ , $\text{PO}_4^{3-}$ , $\text{NO}_3^-$	Detector System
$\text{SO}_4^{2-}$ , $\text{ClO}_3^-$ , $\text{S}^{2-}$ , $\text{SCN}^-$ , $\text{CN}^-$	conductivity
$\text{NO}_3^-$ from $\text{ClO}_3^-$	electrochemical
	uv

\*MMA is the monomethylamine ion

## HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The first step in the scheme for the analysis of organic based explosives is to wash the debris with an organic solvent, such as acetone. After concentration and/or clean-up the sample is ready for analysis by HPLC.

HPLC is an excellent method for the separation and identification of explosives and has the capability for use in the area of quantitative analysis. The high sensitivity of HPLC lends itself well to explosive analysis in forensic matters, because as we have already noted, in bombing cases post-blast residues of big explosives usually are only found in trace quantities.

Another asset that makes HPLC an excellent technique for explosive analysis is that some or-

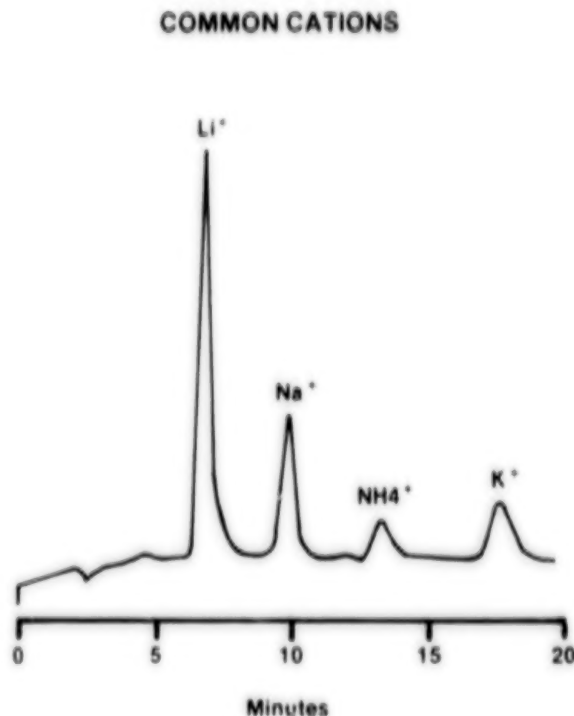


Figure 7. Separation of Common Cations. Eluent: 0.01N HCl/30% MeOH Column: Standard Dionex Separator Column. Peaks: Li<sup>+</sup>, 10ppm; Na<sup>+</sup>, 10ppm; NH<sub>4</sub><sup>+</sup>, 10ppm; K<sup>+</sup>, 10ppm.

ganic explosives are thermally unstable making GC analysis difficult. HPLC, however, can be run at ambient temperatures nullifying this problem.

## Instrumentation

The instrumentation of the IAU is a Waters Liquid Chromatography System equipped with a Model 6000A chromatography pump and a 10 ul sample loop. The system utilizes a Waters Model 440 dual wavelength absorbance detector operating at 282 and 254 NM.

In addition, the IAU has also adopted a Kratos variable wavelength ultraviolet detector at 210 NM and a Thermal Energy Analyzer (TEA) detector to the HPLC system. Figure 8 shows a block diagram of the HPLC set-up utilized by the IAU.

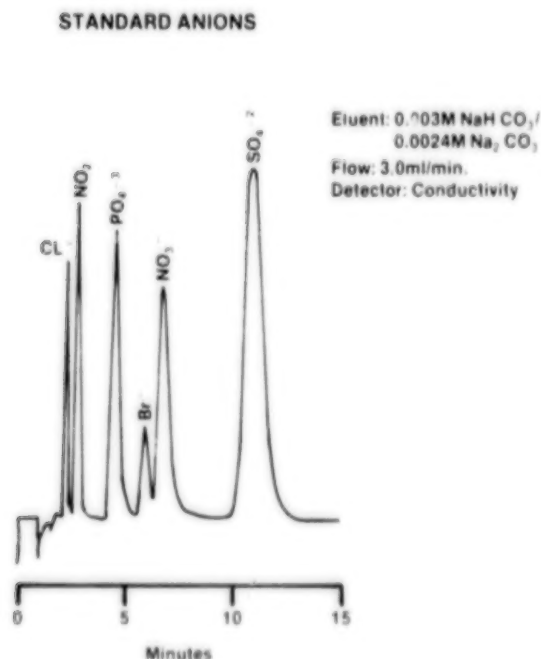


Figure 6. Separation of Common Anions. Peaks: Cl<sup>-</sup>, 4ppm; NO<sub>2</sub><sup>-</sup>, 10ppm; HPO<sub>4</sub><sup>2-</sup>, 50 ppm; Br<sup>-</sup>, 10ppm; NO<sub>3</sub><sup>-</sup>, 30ppm; SO<sub>4</sub><sup>2-</sup>, 504ppm.

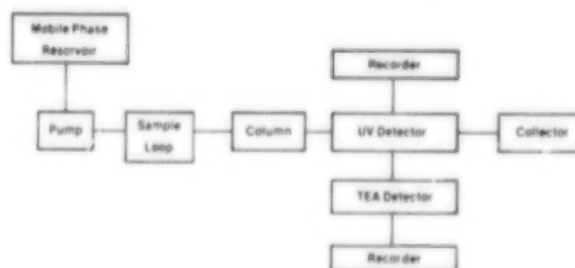


Figure 8. Block Diagram of HPLC Set-Up.

In explosive analysis both reverse phase and normal phase HPLC systems are used. The general conditions of both systems are shown below:

reverse phase conditions

mobile phase: acetonitrile/  
water (65/35)

column: Waters u-Bondapak  
(3.9 mm x 30 cm)

normal phase conditions

mobile phase: methylene chloride/  
1S0-octane (50/50)

column: Waters uPorasil  
(3.9 mm x 30 cm)

### Applications

There are four basic applications of HPLC to explosive analysis as applied by the IAU. They are as follows:

- (1) Trace analysis of explosives in both pre- and post-blast situations.
- (2) Identification and comparison of pre-blast explosives
- (3) Identification and comparison of smokeless powders
- (4) Head space analysis

There are two aspects of trace analysis; post-blast and pre-blast. Figure 9 shows the separation of four different common explosives which can be used as an explosive screen. An unknown explosive would be seen under the exact same con-

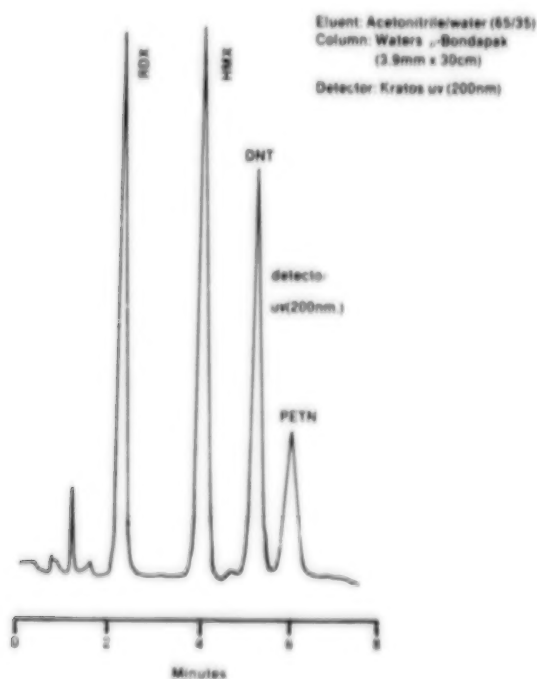


Figure 9. HPLC of Explosive Screen.

ditions and the retention times compared.

Figure 10 shows a liquid chromatogram from an actual case. In this case the liner of a carrying case or bag was suspected of being used to carry explosives. Figure 10 shows the methylene chloride extract of the bag liner. When using the uv detector at 254 nm, no traces of NG or EGDN, two explosives found in dynamite, could be found in the complex matrix which included several plasticizers.

Figure 11 shows the same methylene chloride extract analyzed using the TEA detector. Not only was EGDN and NG found but also traces of PETN. The TEA detector is a -NO<sub>2</sub> functional group specific detector and little of the complex matrix seen in Figure 10 was detected.

HPLC is also used to identify and compare materials that are known or believed to be explosives. Figure 12 shows the chromatogram of a dichloroethane extract of Unigel dynamite. This chromatogram might be compared with the chromatogram of another dynamite extract to determine if they are the same. These type of comparisons are important in association with various explosives with terrorist groups which often use the same explosive in several different bombings. HPLC is a very valuable tool to make these comparisons.

HPLC is also used as the main method of analysis for head space examinations. Figure 13 is a chromatogram of a head space sample taken from the bombing debris of an actual case. It was determined from the chromatogram that dynamite was the explosive used in the bombing.

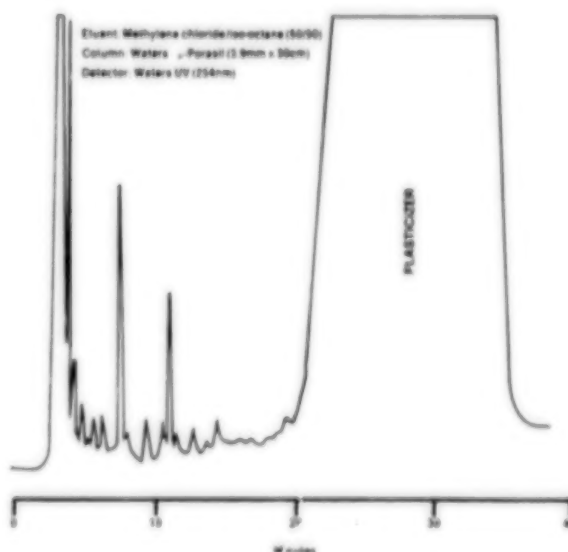


Figure 10. HPLC of Bag Liner Solvent Wash Using UV Detector.

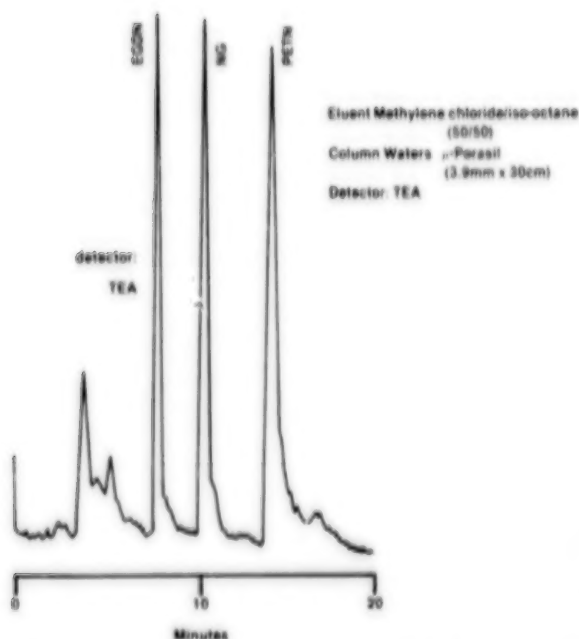


Figure 11. HPLC of Bag Liner Solvent Wash Using TEA Detector.

### GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

The last instrumental method to be highlighted is GC/MS. As can be seen in Figure 1, GC/MS fits in the general scheme of explosive analysis one of two ways. It can either be the next step after the clean-up procedure or it can be the final step after

the HPLC analysis. In this capacity it would serve directly as a confirmation technique. It is in this manner that GC/MS is primarily used by IAU. In either capacity GC/MS is a valuable tool in explosive analysis and can provide a great deal of structural and compositional information about the sample.

### Instrumentation

While the FBI Laboratory has available for its use several GC/MS systems in the IAU, the instrument primarily used is a Hewlett-Packard 5982A Dual Source GC/MS. The GC is a Hewlett-Packard 5710A. Two different columns are used in the GC; one, a non polar column, 2mm x 74 cm, packed with 2% SP-2100 on 100/120 mesh Supelcoport; the other column, one of moderate polarity, is also a 2mm x 74 cm glass column packed with 3% SP 2250 on Supelcoport.

In the MS system the ionization sources are as follows: for electron impact (EI) is 70 eV; while the chemical ionization source (CI) is methane. The mass analyzer is a quadrupole; while the detector is an electron multiplier.

### Applications

There are four basic applications of GC/MS to explosives. Each will be briefly noted.

The first application is the analysis of unknown compounds. GC/MS can supply compositional and structural information about the material. This application is most often used after the clean-up of the organic solvent most common and

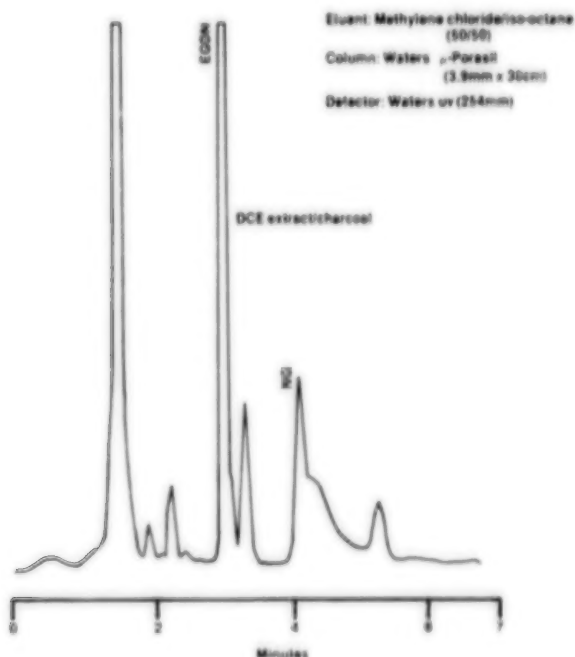


Figure 12. HPLC of Hercules Unigel Dynamite Wash.

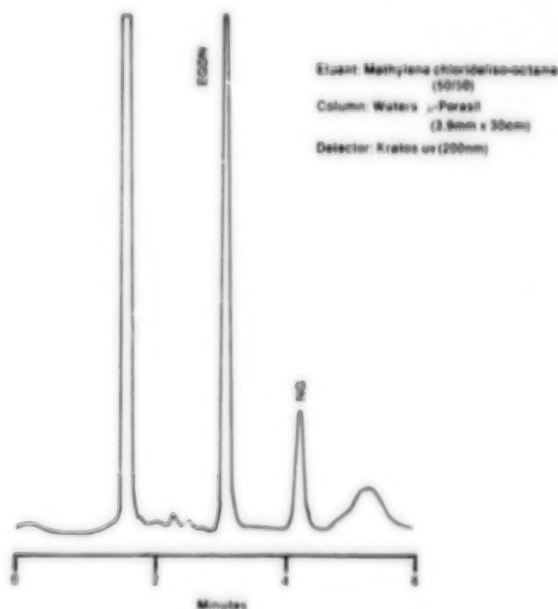


Figure 13. HPLC of Dynamite Head Space.

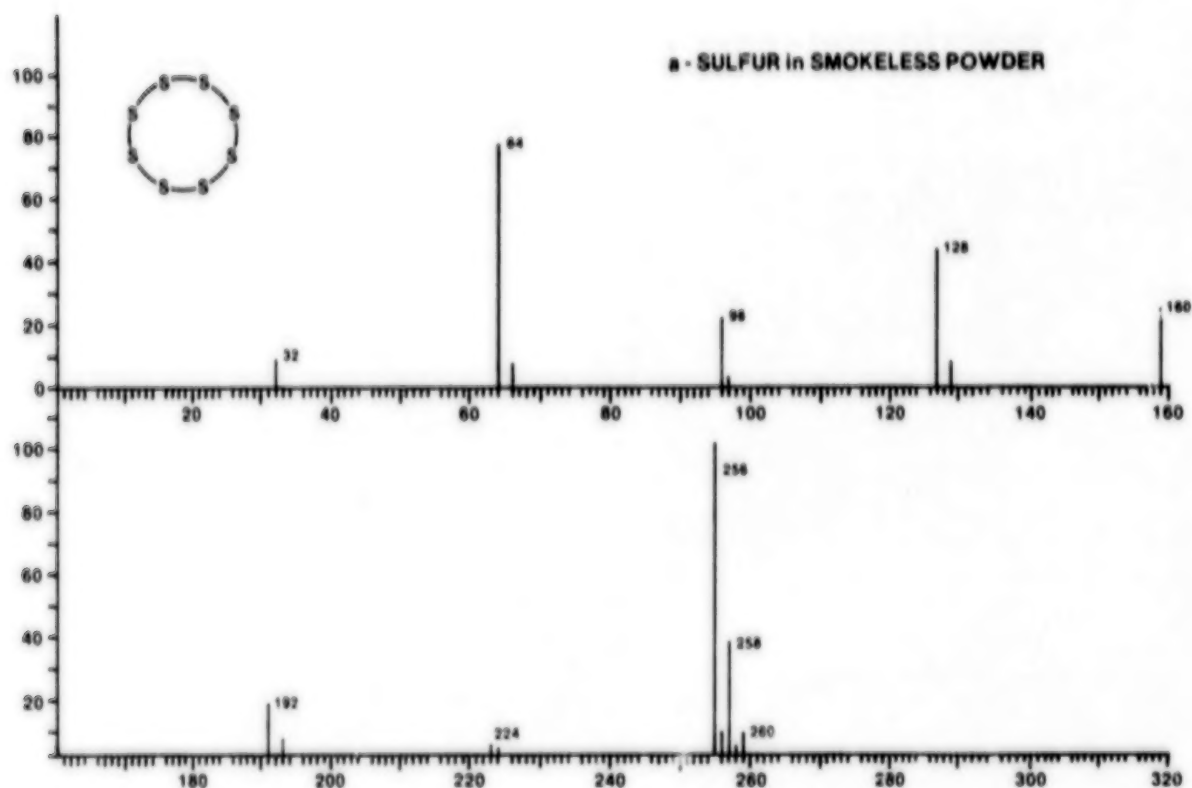


Figure 14. GC/MS of sulfur in Smokeless Powder.

traditional use of GC/MS in explosive analysis.

A second application is with head space and trace vapor analysis. Earlier in this paper the head space analysis procedure was outlined. Instead of the final analysis step being HPLC, it can be GC/MS.

Another application of GC/MS is the analysis of solid and HPLC fractions by direct probe. In this application GC/MS is used as a conformity technique of an HPLC analysis. Figure 14 shows the direct probe mass spectrum of an LC fraction of a smokeless powder specimen. The mass spectrum is that of sulfur.

A fourth application of GC/MS to explosives is the analysis of hydrocarbons. This analysis becomes important when examining such explosives as ANFO, ammonium nitrate and fuel oil. Figure 15 shows the total ion spectrum of a fuel oil found in a homemade ANFO explosive. The identification and characterization of the fuel oil becomes important if the same material consistently is used by terrorist group because it could become a trademark or means of establishing the identity of the group in unclaimed bombings.

In conclusion, the IAU has been using the scheme which has been highlighted in this paper for almost two years with a great degree of suc-

cess. In every instance the scheme may not be religiously followed as it is only meant to be a general guide. It is especially useful for someone who is just starting out in the field of explosive analysis. It should also be noted these are the methods of preference of the IAU and other techniques, such as IR, TLC, GC and DTA are all also useful and can be excellent techniques for explosive analysis.

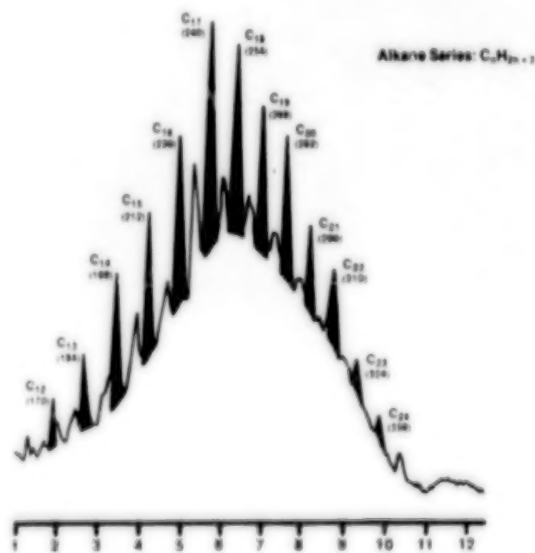


Figure 15. GC/MS of Fuel Oil found in ANFO Explosive.

# NONIDEAL DETONATION BEHAVIOR OF SUSPENDED EXPLOSIVES AS OBSERVED FROM UNREACTED RESIDUES

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**ABSTRACT.** An investigation was conducted by the Bureau of Mines to recover, collect, and identify the solid explosion products of commercial explosives. These condensed products can include unreacted, partially reacted, and completely reacted ingredients. Various unconfined commercial explosives were fired suspended in a sphere in air. The solid residues were collected and studied. Unexpectedly large amounts of residues were found. In general, the granular explosives produced more residue than the simigels and water gels. Many of the residues were found to be thermally reactive, not unlike the original explosives, when they were evaluated by thermal analysis test. The residues from the water gel explosives were the least reactive themally. Preferential consumption of the ingredients was indicated by wet chemical analyses of a few of the residues. Residues were also collected from two semiconfined charges and one confined charge fired in cannon tests. As expected, the amounts of these residues were much smaller. A good inverse correlation was found between the amount of unreacted residue and the square of the ratio of unconfined and confined detonation velocities,  $(D_{\text{unconfined}}/D_{\text{confined}})^2$ , in agreement with the hydrodynamic theory of detonation.

## INTRODUCTION

Coal mine atmospheres contain coal dust and methane (natural gas), which can be ignited, or even exploded, under certain conditions. The explosives used in coal mining are possible ignition sources, and therefore they are required to undergo and pass a battery of incendivity tests before they can be approved for use in underground coal mines.

High pressures, shock waves, high-temperature gaseous products, and hot condensed particles all result from a detonation of an explosive charge. They can all singly or collectively ignite a dusty and gaseous atmosphere, if they possess the required energy. Whereas the ability of shock waves and of hot gases to ignite flammable coal mine atmospheres has been studied in some detail, the specific role of hot condensed particles in the ignition process of coal mine atmospheres has not been assessed to the same extent. Hot condensed

particles can be viewed as hot surfaces supplying energy, or as catalytic surfaces enhancing the ignition process, for example, by releasing oxygen while decomposing.

It was presumed that at least some of the hot particles would remain as a solid residue, and therefore it was decided to collect and observe the condensed residues from various explosives.

## EXPERIMENTAL WORK

### Instrumentation—Suspended Shots

A large steel sphere, 3.7 m in diameter, with suitable hardware was modified and used for detonating the explosive charges and for containing the residues. The inside surface of the steel sphere was metallized with aluminum and in general withstood the effects of the explosions' gaseous and condensed products.

A vacuum pump with an in-line 5-micrometer sintered brass filter was used in a large number of the tests for removal of the gaseous explosion products. In later tests a circulating pump was used to remove the gaseous products and intro-

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duce fresh air into the sphere.

A vacuum cleaner, fitted with a new, preweighted, paper bag for each test, was used to collect the powdered residues.

### Materials

A variety of commercial explosives, which included granular, gelatinous, and water gel formulations, was tested.

The granular and gelatinous formulations contain explosive oils such as mixtures of nitroglycerin with ethylene glycol dinitrate; nitrocellulose is another ingredient. In addition, they contain oxidizers and fuels such as ammonium nitrate and wood meal and salts such as sodium chloride. The gelatinous formulations, on the average, contain more explosive oil and nitrocellulose than do the granular formulations. Also, in general, their oxygen balance is closer to stoichiometric, their density is higher, and they are more energetic than the granular explosives.

The commercial explosives tested in this program were chosen from explosives sent to the Bureau of Mines for a variety of permissibility tests. On the whole, the rates of detonation of gelatinous explosives tested by the Bureau of Mines range from 3200 to 5600 m/sec, whereas the rates of detonation of granular explosives range from 1700 to 3500 m/sec.

The water gel explosives do not contain explosive oils or nitrocellulose. They contain salts such as ammonium nitrate, sodium nitrate, and sodium chloride, and other ingredients. All of these ingredients are blended in water, and the mixture is gelled with gelling agents such as guar gum. On the average, their rates of detonation range from 3400 to 3800 m/sec [3].

In most of the suspended tests the weight of the explosive charge, inclusive of the wrapper, was 336 grams, but some smaller and a few larger charges were also evaluated. When more than one cartridge was used, the end, or ends, of each cartridge was cut off, as necessary, and the cut ends were firmly butted together and taped with a strong tape. A few charges that were more fluid in consistency were wrapped in an additional wrap of lay-flat, seamless, polyethylene tubing, or were carefully transferred from the original wrap into the polyethylene tubing. The diameter of all the charges was 3.2 cm (1 1/4 inches), and their length ranged from about 27.7 cm to 40.6 cm, dependent on the density and weight of the explosive charge. In the tests using only one cartridge (charge weight

less than 200 grams), the charge length was about 20 cm.

### Initiator

A No. 8 detonator was used in all the tests; it was completely inserted in one end of the charge.

## RESULTS

The average amounts of solid residue collected from each explosive fired in the sphere in the suspended mode are presented in Table 1, as recovered weight-percent of initial total weight. On the average, 55 to 60 pct of the granular-type explosives were recovered. In the case of the gelatinous charges similarly fired, about 30 to 40 pct remained as condensed residue. A larger spread in the amount of recovered residue was found for the water gels; it ranged between 13 and 46.5 wt-pct, and the average was about 32.

To the eye, essentially all the residues appeared as fine, grey or beige-grey powders. Large prills, globs of gelatinous explosive oil, or crystals of such ingredients as ammonium nitrate, sodium nitrate, or sodium chloride, all of which are easily discerned by the unaided eye in many of the original formulations, were not observed in the collected residues. When the residues were sieved, the major portion of shredded wrapper was found in the coarser sieves, while the explosive residue powder was found in the finer fractions. Most of it passed through sieve No. 40 (opening  $\cong$  0.425 mm). The portion of powder retained on sieves 20, 30, and 40 did contain white grains, as well as some powder. The residues also contained extraneous material from the detonator and from the vacuum cleaner brushes. This foreign material was carefully removed with tweezers.

Most of the tests were done when the humidity was low, in order to avoid dissolution of the residues, due to adsorption of moisture by the highly hygroscopic materials, such as ammonium nitrate, found in many of the residues. The sphere was thoroughly washed and dried between most tests and after each test in which the residue could not be collected due to the humidity.

### Residues of the Explosives as Related to their Detonation Velocities

The hydrodynamic theory of detonation, and more specifically the grain-burning mode of reaction, was used to explain the results. According to this model of explosive reaction, the portion of the explosive that undergoes complete detonation,



**Table 1. AMOUNT OF RESIDUE COLLECTED IN SPHERE FROM SUSPENDED EXPLOSIVES FIRED IN AIR**

Explosive type and key number		Residue, wt-pct (unreacted portion)
Granular:		
	1792	59.3
	1794	37.6
	1847	66.9
	1914	63.6
	2002	62.4
	<sup>1</sup> 2015	39.7
	Average	54.9
Gelatinous:		
	1649	37.3
	1906	32.3
	1930	35.8
	1971	41.3
	Average	36.7
Water Gels:		
	1732	37.3
	1749	30.5
	1787	28.7
	1810	39.5
	1857	46.5
	1862	29.5
	<sup>2</sup> 1952	13.0
	<sup>1,2</sup> 2014	20.5
	2019	42.4
	Average	32.1

<sup>1</sup> Taggant particles added to explosive for ease of identification; 0.05 wt-pct of total explosive weight.

<sup>2</sup> Key Nos. 1952 and 2014 are the same explosive; variation in results for the two key numbers may be due to differential aging brought about by unequal storage time (a lower key number signifies longer storage time), to differences in composition from manufacturing process, or to the presence of taggant particles (explosive batches containing taggant were specifically prepared for tests by the Bureau of Mines, PRC, and may have been formulated on a small scale).

designated  $m$ , is a function of detonation velocity as follows:

$$m = \left[ \frac{D}{D_{\infty}} \right]^2 \quad [1]$$

In this relationship,  $D_{\infty}$  is the maximum attainable detonation velocity (theoretically attainable at infinite charge diameter), and  $D$  is the actual detonation velocity. In our experiments, we can equate the collected residue with the unreacted portion, or  $1 - m$ .

The detonation velocities of some of the explosives used in our residue collection tests were

measured in two configurations. In one configuration the charge diameter was 3.2 cm (1 1/4 inches)—identical to the size of the charges used for residue collection—and it was not confined (except for the lightweight paper or plastic wrapper). This velocity is designated as  $D_{1/4}$ . In the other configuration, Schedule 80 steel pipe [7.6-mm (0.300-inch) wall thickness] was used to confine charges 7.6 cm (3 inches) in diameter. This resultant detonation velocity is designated  $D_3$ . The results of these measurements are presented in table 2 and in Figure 1, in which  $(D_{1/4}/D_3)^2$  values are plotted as a function of the portion of explosive that reacted. Although the  $D_3$  values are probably smaller than  $D_{\infty}$  values in most of the cases cited here, they are deemed close enough to their respective  $D_{\infty}$  values to be fair approximations. To better approximate the  $D_{\infty}$  values would have required much larger amounts of explosives and special facilities for testing such amounts. Theoretical values of  $D_{\infty}$  are based on various assumptions—including the choice of equation of state to be used in calculating these values—and do not always agree with experimental values. Therefore, they were not used here.

Good agreement exists between the  $m$  values obtained from the residues, and from the  $(D_{1/4}/D_3)^2$  results, for the granular explosives. Relatively good agreement can be seen for the respective water gel values, whereas for the gelatinous explosives there is the least but still fair agreement.

## CHEMICAL ANALYSIS OF THE RESIDUES

Chemical analysis of explosives is usually done by standard wet chemistry methods. The type of explosive and its ingredients determine the solvents used to extract and separate the various chemicals, the order of extraction, and the analytical procedures. The relatively large amounts of residues collected implied the presence of unreacted ingredients, as well as of partially reacted ingredients, from the original formulations. Based on this assumption, standard procedures for analysis of unfired explosives were utilized for the chemical analysis of residues as well. However, methods other than those usually utilized in the routine analysis of explosives at the Bureau of Mines were employed, as needed, for compounds not commonly present in explosives. These methods included atomic absorption and atomic emission spectroscopy, X-ray diffraction and infrared spectroscopy, and scanning electron microscopy.

**Table 2. DETONATION VELOCITIES FOR THE VARIOUS TEST EXPLOSIVES AND RESIDUES COLLECTED FROM THESE EXPLOSIVES WHEN FIRED SUSPENDED IN AIR**

Explosive type and key number	Detonation velocity, m/sec		$\left[\frac{D1\frac{1}{4}}{D_3}\right]^2$	Residue, wt-pct (unreacted portion)	Portion reacted, m
	D1¼ (original wrapper)	D3 (steel tube)			
Granular:					
1792	2,375	3,835	0.38	59.3	0.41
1914	2,070	3,309	.39	63.6	.37
2002	2,308	4,286	.29	62.4	.38
Average	—	—	.35	61.8	.39
Gelatinous:					
1649	5,000	6,000	.69	37.3	.63
1930	5,422	6,002	.82	35.8	.64
1971	5,005	5,294	.89	41.3	.59
Average	—	—	.80	38.1	.62
Water gels:					
1749	3,750	4,500	.69	30.5	.69
1857	3,000	4,390	.47	47.1	.53
1862	3,529	4,577	.59	29.5	.70
2014	3,565	4,737	.57	20.5	.79
2019	3,750	4,821	.61	42.4	.58
Average	—	—	.59	34.0	.66

### CHEMICAL ANALYSIS RESULTS

The main goal of the chemical analysis was to identify and quantify unreacted explosive ingredients, partially reacted ingredients, and end products of completely reacted ingredients, and in this way to determine if preferential reaction of the various ingredients occurred, and to what extent.

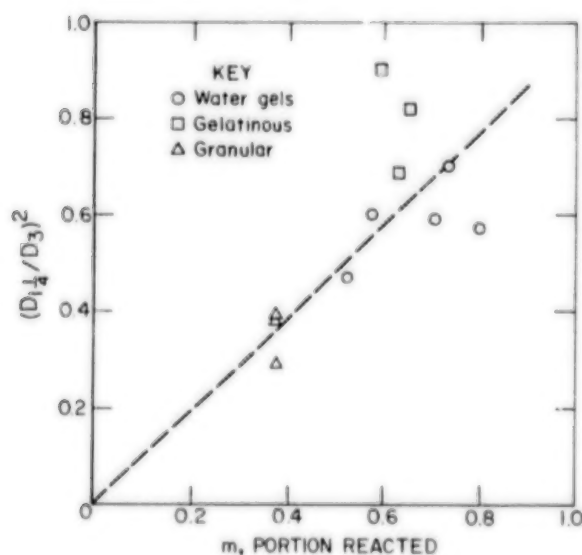


Figure 1. The Square of the Ratio of Detonation Velocities versus Portion of Explosive That Reacted.

Information of this kind can contribute to a better understanding of the actual detonation behavior of heterogeneous explosive formulations; in addition, some insight into the possible incensive behavior of the different ingredients of such formulations, as they undergo changes during and following the detonation, might be gleaned from such an account.

The analyzed residues are identified by test number as presented in Table 1A in the Appendix. Results of the analyses are shown in Tables 3 and 4 as the percent weight of the original ingredients based on the commercially reported compositions. The results of chemical analysis of residues from granular and gelatinous explosives are given in Table 3, while Table 4 presents analysis results of one residue from a water gel slurry explosive.

As can be seen in Table 3, the explosive oil was not recovered in any of the residues analyzed. Also, on the average, ammonium nitrate was recovered in smaller quantities, percentagewise, than was sodium nitrate, based on original amounts. Water and nitrocellulose were present in the original explosives in very small quantities, so that small errors in analysis can lead to large errors in the values of percent recovered. Hence, these values can be disregarded. Also, moisture is easily picked up by residue ingredients, such as

**Table 3. PERCENT WEIGHT OF ORIGINAL <sup>1</sup> EXPLOSIVE INGREDIENTS RECOVERED IN RESIDUES FROM GRANULAR AND GELATINOUS EXPLOSIVES**

	Test 15	Test 20	Test 21	Test 23	Test 32
Key Number . . . . .	1906	1906	1794	1792	1930
H <sub>2</sub> O	37	24	89	93	73
Explosive Oil	0	0	0	0	0
NH <sub>4</sub> NO <sub>3</sub>	25	17	32	47	22
NaNO <sub>3</sub>	61	72	~ 101	~ 105	60
NH <sub>4</sub> Cl	<sup>2</sup>	<sup>2</sup>	<sup>2</sup>	<sup>2</sup>	101
NaCl	34	37	57	87	<sup>2</sup>
CaCO <sub>3</sub>	38	27	15	29	168
C.C.M. <sup>3</sup>	56	43	43	50	83
Nitrocellulose	179	72	<sup>2</sup>	<sup>2</sup>	0
Wrapper, paper	<sup>4</sup>	<sup>4</sup>	39	55	<sup>4</sup>
Wax	<sup>4</sup>	<sup>4</sup>	39	40	<sup>4</sup>

<sup>1</sup> Based on chemical analysis by the Bureau of Mines, PRC

<sup>2</sup> Not present in original formulation.

<sup>3</sup> Combustible carbonaceous material.

<sup>4</sup> Not analyzed.

ammonium nitrate, and will affect the results for water.

The results in Table 4 for a residue collected from a water gel explosive (Test 27) are in many respects of a similar nature to the results shown in Table 3. That is, some ingredients, such as amine nitrates, were not recovered at all. Others were found in the original form as well as in decomposed form. For instance, both calcium nitrate and its insoluble decomposition product, calcium oxide, were recovered. Nitrite ion was found in the

**Table 4. PERCENT WEIGHT OF ORIGINAL <sup>1</sup> EXPLOSIVE INGREDIENTS RECOVERED IN THE RESIDUE OF A WATER GEL EXPLOSIVE**

Key No. . . . .	Test 27 1810
Mode of Test . . . . .	Suspended
H <sub>2</sub> O	32
Amine nitrate sensitizer	0
NH <sub>4</sub> NO <sub>3</sub>	0
NaCl	72 as NaCl 22 as NaNO <sub>3</sub>
Ca(NO <sub>3</sub> ) <sub>2</sub>	27 as Ca(NO <sub>3</sub> ) <sub>2</sub> 25 as Ca(NO <sub>2</sub> ) <sub>2</sub> 25 as CaO
Aluminum	96
C.C.M.	30 <sup>2</sup>

<sup>1</sup> Based on commercially reported compositions.

<sup>2</sup> Contains plastic wrapper and guar gum which were not analyzed separately.

residue and was "assigned" as calcium nitrate, an intermediate decomposition product of calcium nitrate, although calcium nitrite itself was not identified as such. Sodium nitrate, not an original ingredient, was found in the residue as well. Infrared and X-ray diffraction spectroscopy were used in an effort to verify the presence of the sodium nitrate and the various calcium compounds. Sodium nitrate peaks were prominent in the X-ray diffraction spectra, as were peaks of sodium chloride and aluminum, whereas calcium compounds were not observed. The infrared spectrum did not contain well defined peaks of any of the calcium compounds in the residue, but the overall spectrum resembled spectra of hydrated calcium nitrate compounds. Finally, scanning electron microscopy (SEM) was utilized to observe the residue particles visually, and see if, possibly, the calcium compounds were amorphous and therefore were not seen in the X-ray spectra. Cubic crystals of sodium chloride were the only identifiable crystals. Their sizes were roughly between 1 and 10  $\mu$ m. Some clusters that appear to be particles stuck together by surface melting were also observable. Fusion, undergone by some portions of the residue, is evident in the SEM micrographs of higher magnifications. Particles of similar appearance were observed in residues from Tests 24 and 28, utilizing the same explosive as in Test 27. The residue from Test 28 was partially analyzed. Compositions of the residues from Tests 27 and 28

were similar, including the presence of sodium nitrate in both.

### THERMAL ANALYSIS OF THE RESIDUES

Thermal analysis is very helpful in the identification of single compounds, via their melting temperature, or the temperature of solid phase changes that they undergo. In the case of a mixture of two compounds that do not react chemically or form a eutectic, thermal analysis is also of aid. When more than two compounds are present in a mixture, thermal analysis is utilized mainly for assessing the overall thermal behavior of the mixture.

The instruments used in thermal analysis are sensitive and respond best to small samples, of the order of a few milligrams. The explosives are heterogeneous mixtures containing both liquids and solids, the latter of varying sizes. The residues are also multicomponent solid mixtures. Larger samples are required for good representation, and samples of about 50 mg were utilized.

A Du Pont 990 differential scanning calorimeter (DSC) (reference to specific makes and models of equipment and suppliers is made for identification purposes only and does not imply endorsement by the Bureau of Mines) was employed in the thermal tests, which were done in an atmosphere of static air, at a heating rate of 10° C/min. Fine glass beads were used as reference material. A quantitative thermal analysis was not sought here, only an overview of thermal behavior of the original explosives versus their resultant residues.

### THERMAL ANALYSIS RESULTS

A gelatinous-type explosive (Key No. 1906) used in Tests 15 and 20 was evaluated in the DSC. A thermogram of a small sample of this explosive appears in Figure 2, thermogram A. A small sample of the residue of Test 15 gave the thermogram B which is seen in Figure 2, whereas thermogram C in Figure 2 is for a larger sample of the same residue. A large sample of residue was utilized to obtain the thermogram for the residue from Test 20, which is seen in Figure 2, thermogram D.

Another gelatinous explosive (Key No. 1930) was used in Test 32; its thermogram is shown in Figure 3, thermogram A, while the residue from this test gave thermograms B and C in Figure 3 for a large and small sample, respectively.

Two granular explosives, Key Nos. 1794 and 1792, were evaluated in Tests 21 and 23, respec-

tively. Thermograms of the original explosives were not obtained because the explosives were not available any more. Thermograms of the residues are shown in Figure 4; thermogram A was found for Key No. 1794 and thermogram B is for Key No. 1792.

In addition to gelatinous and granular explosives, water gel explosives were also tested. One water gel explosive, Key No. 1810, was fired in Tests 27 and 28. Figure 5, thermogram A was obtained for the original explosive, while thermograms from the residues of Tests 27 and 28 are depicted in thermograms B and C of Figure 5, respectively (Disregard thermogram D as it does not pertain to this discussion.) Finally, another water gel explosive, Key No. 1942, fired in Test 36 has the thermograms shown in Figure 6, thermogram A and B, for the original formulation and for the residue, respectively.

### DISCUSSION OF RESULTS

Preferential consumption of the explosive ingredients was indicated in the residues that were analyzed. For example, explosive oil (usually nitroglycerin with ethylene glycol dinitrate) was consumed completely, while other ingredients such as ammonium nitrate, sodium nitrate, and sodium chloride were only partially consumed or decomposed to various degrees. The large amounts of residues recovered were unexpected. Also unexpected was the fact that ingredients such as ammonium nitrate which decompose at low temperature remained partially unreacted. Sodium nitrate, which decomposes at a higher temperature, for the most part did not take part in the detonation and was recovered almost intact (60 to 100 wt pct of the original sodium nitrate was found in the analyzed residues from the suspended shots).

Although the possibility of incomplete reaction is cited by the many research workers in the explosives field, not much detailed information is available on the subject. Therefore comparisons are difficult. Beyling and Drekonf (*1*) observed appreciable amounts of unexploded ingredients in the products of commercial blasting agents tested in actual field conditions. The composition of the unexploded portion was reported by them to be similar to the composition of the original formulation.

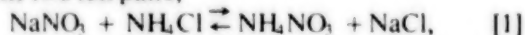
Craig *et al.* (*2*) measured detonation rates of a confined water gel explosive, using 10.16- and 20.23-cm-diam clay pipes. The experimental detonation rates were much lower than the theo-



retically calculated values. Residues were not collected by Craig *et al.*; however, they propose incomplete reaction as the explanation for the differences between the measured and calculated detonation velocities. Furthermore, their calculated, theoretical detonation rates do agree with experimental values when it is assumed that ammonium nitrate failed to react in the sample of larger diameter. Similarly, for a good agreement between theoretical and experimental detonation rates for the small size charge, one has to assume that other ingredients, in addition to ammonium nitrate, do not react completely.

The concept of "ion exchange" has been evoked to explain the less incensive behavior of explosive formulations containing sodium nitrate and ammonium chloride in flammable coal mine atmospheres.

The two ion pairs,



are theoretically equivalent as far as the total available energy that can be released by each pair in a detonative reaction is concerned. But if each salt reacts at a different rate, so that its contribution to the total energy released in the detonative reaction zone (ahead of the C-J layer) is different, then these pairs are not equivalent, especially when the explosive charge is not confined and portions of the ingredients do not react at all.

The presence of sodium nitrate in two residues from one water gel explosive (Key No. 1810) not containing sodium nitrate as an original component raises some questions about the actual compositions of water gels at the time that they are fired. Although it is not conclusively known if the sodium nitrate was formed in the detonation, or was present in the original explosive charge, the latter is thought to be the case. Ammonium nitrate and sodium chloride can undergo metathesis, or double decomposition, as follows:



This reaction could occur in storage during temperature changes which affect the solubilities of the various salts. And indeed results from other, unrelated tests suggest that sodium nitrate is present in the original explosive prior to detonation. In the winter months, when temperatures are low, the solubility of sodium nitrate decreases and it can precipitate out inside the water gel.

Anhydrous calcium nitrate melts at  $\sim 561^\circ\text{C}$  and at temperatures higher than the melting point decomposes to the nitrite by evolving oxygen. On further heating to higher temperature, calcium

oxide forms, concurrent with evolution of nitrogen oxides. Consideration of the results in Table 4 leads to the conclusion that a portion of calcium nitrate undergoes complete reaction to calcium oxide when it is a constituent of a water gel explosive that is fired in a suspended, unconfined mode. We can reasonably surmise that increased confinement will increase the amount of calcium nitrate

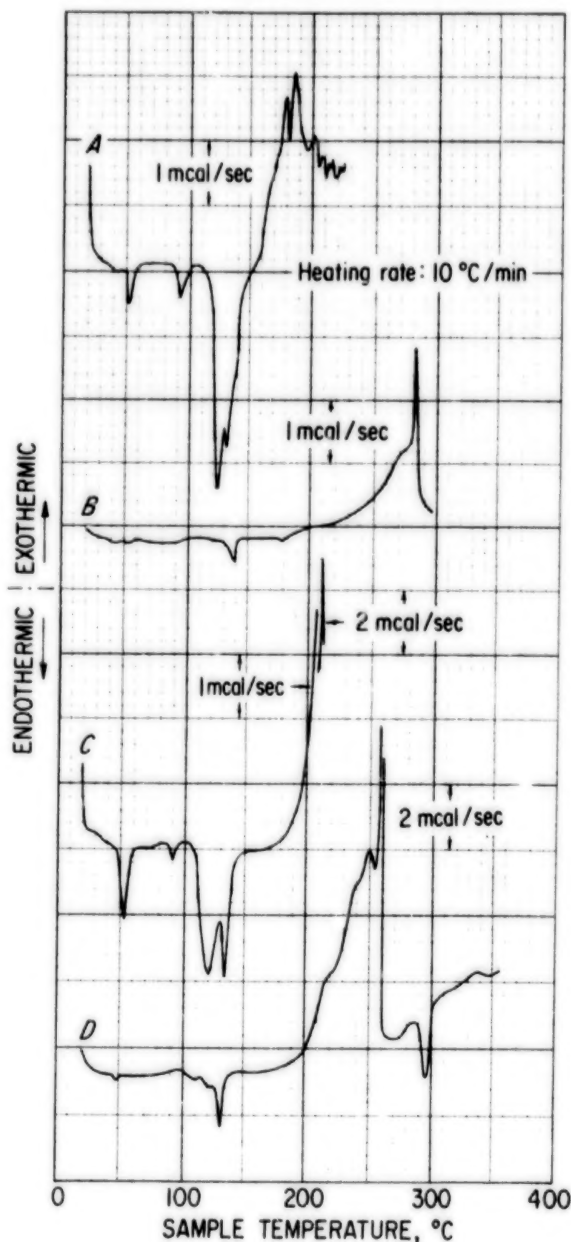


Figure 2. Thermograms of a Gelatinous Explosive (Key No. 1906) and of its Residue.

A. Original composition.

B. Residue; Test 15 (fine powder from sintered filter in vacuum pump line).

C. Residue; Test 15.

D. Residue; Test 20.

that is converted to the oxide.

Fine aluminum powder, when a component of an explosive formulation, is considered as a contributor to the incandive behavior of the explosive. It can burn in air to form aluminum oxide and release large amounts of energy in the process. But most of the aluminum from the explosive fired in Test 27, unconfined, was recovered in the residue unchanged.

We have checked for the presence of nitrite in the analyzed residues that contained sodium nitrate as an original ingredient, but did not detect any in spot tests. A more careful analysis is needed, because many of the ingredients found in the residues interfere in the tests for nitrite.

Although the residues differ in composition from the original formulations, many of them

possess a combination of ingredients that is exothermic, as shown by the thermograms in Figures 2 and 3 for two gelatinous explosives. Without going into great detail about the various aspects of the thermograms, we can say that the residues are quite similar in thermal behavior to the parent compositions; the only difference of importance is the temperature at which exothermic behavior is initiated. The temperature of initiation of exothermic behavior is lower for the original explosives than for their respective residues. Thermograms of residues from two granular explosives, comparable in composition, are presented in Figure 4. The parent explosives were not available any more when the thermograms were obtained,

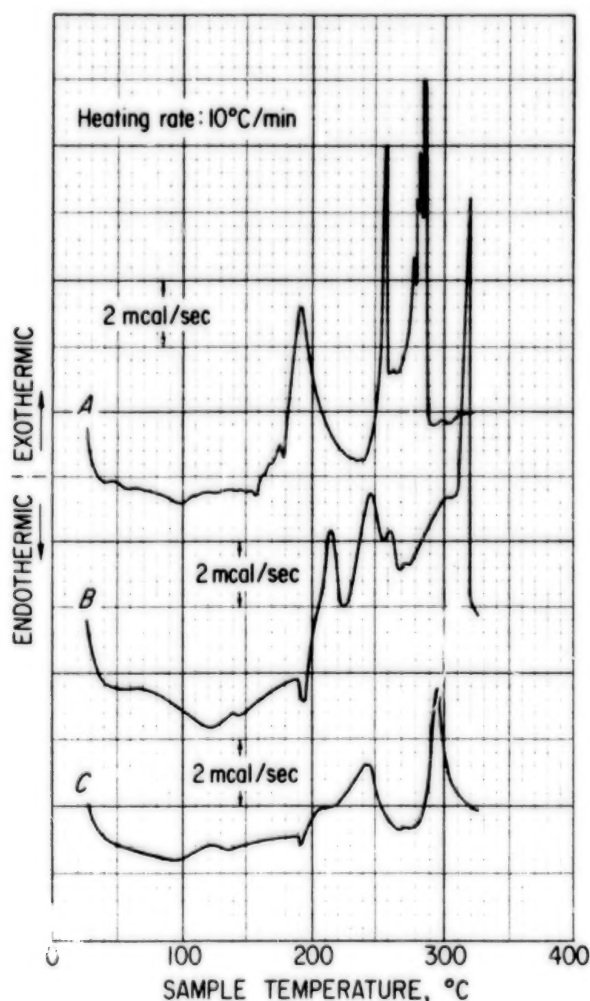


Figure 3. Thermograms of a Gelatinous Explosive (Key No. 1930) and of its Residue.

- A. Original composition.
- B. Residue; Test 32, Large sample.
- C. Residue; Test 32, Small sample.

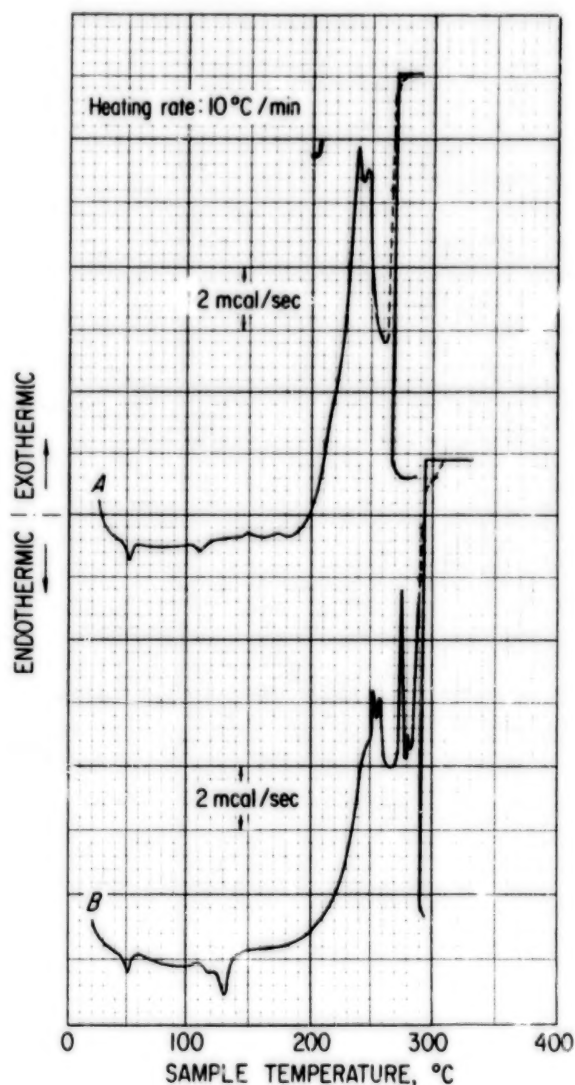


Figure 4. Thermograms of the Residues of Two Granular Explosives. (a) Key No. 1794; (b) Key No. 1792.

- A. Residue; Test 21, Key No. 1794.
- B. Residue; Test 23, Key No. 1792.



but the thermograms of the residues are similar in most aspects to thermograms of the same explosives, but of different key numbers. This was expected, since one residue contains about 60 percent of the original charge; the other residue contains about 40 percent of the original charge. The high degree of exothermicity is clearly evident in the thermograms. The water gels on the whole have undergone more reaction in our tests, and their residues contain less reactive material. This is evident when the thermograms of the parent explosive and its residue are compared, as in Figures 5 and 6, which are self-explanatory. The thermal analysis results indicate that large amounts of residue, which can accumulate in sites where unconfined granular or gelatinous explosives are fired, can constitute a hazard. On the other hand, in cases of sabotage, if explosives are used in an unconfined mode, they may be more easily detectable. One of the difficulties in identification is their appearance. They look more like soil or dust than like explosives.

### SUMMARY

Chemical analysis of a few of the residues shows that their composition is not identical to the orig-

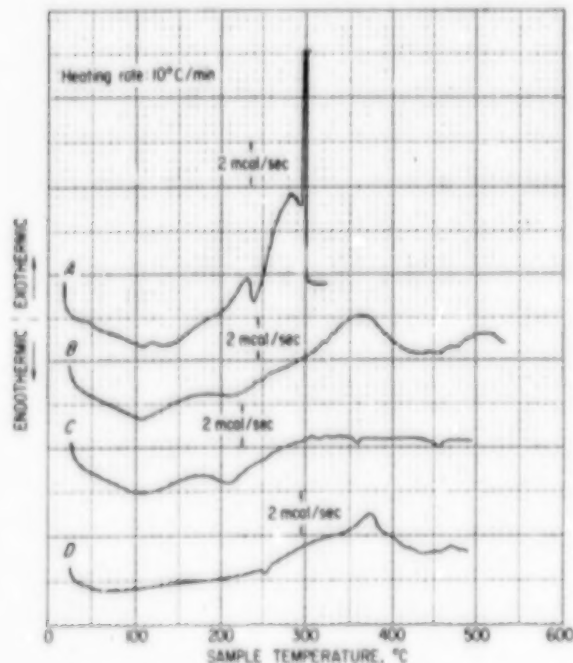


Figure 5. Thermograms of a Water Gel Explosive (Key No. 1810) and of its Residue.

- A. Original composition.
- B. Residue; Test 27.
- C. Residue; Test 28.
- D. Residue; Test 40.

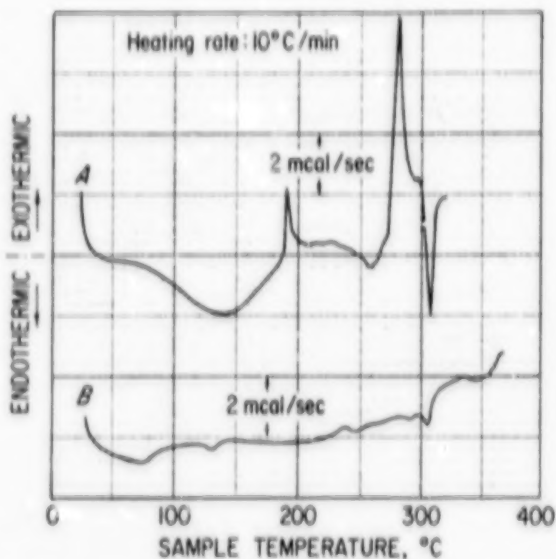


Figure 6. Thermograms of a Water Gel Explosive (Key No. 1952) and of its Residue.

- A. Original composition.
- B. Residue; Test 36.

inal composition. Rather, preferential reaction has been observed. Ingredients such as explosive oil were not recovered at all, while various percentages of most of the other ingredients were recovered. Sodium nitrate was among the least consumed. The presence of nitrite in one residue was gratifying, because it was specifically looked for. The presence of compounds that are formed by different stages of decomposition suggests that consecutive reactions can take place in the explosion process, or its aftermath, and that reaction gases, such as oxygen and nitrogen oxides, evolved during these reactions, may act as sensitizers and enhance the probability of ignition of natural gas, coal dust, or both.

For purposes of recovering residues in cases of sabotage, it would be advantageous to remember that the residues look like soil or dust, and thus are not easy to identify visually. Also, it should be kept in mind that most of the commercial explosives contain ammonium nitrate and/or amine nitrates, all of which are highly hygroscopic. When exposed to the atmosphere, they will adsorb moisture and dissolve. The resultant solutions are usually acidic and in turn can dissolve foreign matter.

The possibility of ion exchange either in storage or in the detonation can interfere in the identification of the original explosive from the analysis of its residue. For this reason some form of tagging for identification is still very appealing.

## APPENDIX

Table 1A. SUSPENDED EXPLOSIVES FIRED IN SPHERICAL CHAMBER IN AIR WITH A NO. 8 DETONATOR <sup>1</sup>

Test No.	Key No.	Explosives tested	Type	Charge weight, <sup>2</sup> g	Residue, wt-pct
15	1906		Gelatinous	185	33
20	"		"	341	26
21	1794		Granular	258	38
22	1857		Water Gel	313	47
23	1792		Granular	289	55
24	1810		Water Gel	336	43
25	"		"	336	36
26	"		"	335	40
27	"		"	336	38
28	"		"	175	40
29	"		"	169	41
30	1906		Gelatinous	342	38
32	1930		"	339	34
34	1862		Water Gel	312	30
36	1952		"	336	10
44	"		"	336	16
46	1787		"	275	29
48	"		"	336	28
50	1732		"	336	37
52	1749		"	336	27
60	1649		Gelatinous	336	35
62	<sup>3</sup> 2015		Granular	336	40
64	1971		Gelatinous	336	41
66	"		"	336	39
72	"		"	336	43
74	"		"	509	42
76	"		"	<sup>4</sup> 336	51
78	1792		Granular	336	64
80	2019		Water Gel	336	42
82	1749		"	336	35
84	<sup>3</sup> 2014		"	336	21
86	2002		Granular	336	63
88	1649		Gelatinous	336	40
90	2002		Granular	336	62
92	1914		"	336	64
94	2014		Water Gel	336	20
96	1930		Gelatinous	336	37
98	1848		Granular	192	67

<sup>1</sup> Key No. C-1832

<sup>2</sup> Charge weight includes the weight of wrapper used in each test.

<sup>3</sup> Taggant added to explosive for identification purposes.

<sup>4</sup> 2.5 g tetryl booster was used.

## ACKNOWLEDGEMENTS

The authors acknowledge Mr. Thomas C. Ruhe for the careful preparation of the sphere facility, and for his valued participation in the experiments. Thanks are due Mr. Charles F. Swab, Jr. for some of the chemical analyses.

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## **INSTRUMENTAL METHODS**

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## INSTRUMENTAL TECHNIQUES UTILIZED IN THE IDENTIFICATION OF SMOKELESS POWDERS. PROTON MAGNETIC RESONANCE (PMR) AND GAS CHROMATOGRAPHY (GC).

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**ABSTRACT.** An approach to identifying the manufacturer of domestic commercial smokeless powders has been evaluated at the Bureau of Alcohol, Tobacco and Firearms (ATF) National Laboratory Center and the Drug Enforcement Administration (DEA) North Central Field Laboratory. The procedure uses a combination of proton magnetic resonance (PMR), and Gas Chromatography (GC). The use of PMR permits discrimination between similar products of the major U.S. manufacturers, namely, Dupont, Hercules, or Winchester-Western. Using PMR alone, some discrimination can be made within a particular manufacturer's products. The GC profile permits the observation of major and minor components. When PMR and GC data are combined types within a single manufacturer can be distinguished. These results were obtained using undetonated samples. This presentation discusses the differences observed in both the PMR spectra and GC chromatograms, including variations seen in products from different manufacturers and those in products from a particular manufacturer. Examples of the results showing both similarities and differences will be given. Potential application of the technique to typical forensic problems is described.

An approach to identifying the manufacturer of domestic commercial smokeless powders has been evaluated at the Bureau of Alcohol, Tobacco and Firearms (ATF) National Laboratory Center and the Drug Enforcement Administration (DEA) North Central Field Laboratory. The procedure utilizes a combination of proton magnetic resonance (PMR), and gas chromatography (GC).

A Forensic Chemist is often asked a question similar to the following: "Is the smokeless powder in the recovered and/or seized pipe bomb the same as that seized from the suspect?" It is apparent that for a definitive answer to this question, there is a need for a comparison method, which is effective both in distinguishing between similar products from different producers and different types produced by a single manufacturer.

References 1 through 8 describe approaches to the examination of smokeless powder; however a definitive identification is not usually addressed. The main thrust of many of the articles is to identify the smokeless powder as having come from a

particular cartridge for gunshot residue examination and not for explosive examinations. Each paper deals with only one aspect of the examination and therefore does not give a definitive product identification. The literature does not deal with the question regarding the identification of the manufacturers of single and double base smokeless powders.

This research was begun to determine the feasibility of utilizing proton magnetic resonance (PMR) and/or gas chromatography (GC) to identify the various smokeless powders available commercially in the United States. It was soon found that each technique gave certain discrete information. The two techniques, in conjunction with a microscopic examination to determine the morphology (Table 1) of the sample allows identification of, not only the manufacturer, but also the various powders produced by the manufacturer, which is illustrated in Figure 1. Thin-layer chromatography was used to determine whether the smokeless powder was single-base (SB) or

**Table 1. MORPHOLOGY OF SMOKELESS POWDERS.**

<b>Improved Military Rifle (IMR)</b>				<b>Non-Perforated Wafer</b>		
DUPONT				DUPONT		
IMR-3031	IMR-4198	IMR-4320		SR-4756	SR-7625	800-X
IMR-4831	IMR-4064	IMR-4227				
IMR-4350	IMR-4895					
HERCULES				HERCULES		
Reloader 7				Bullseye	2400 Red-Dot	Herco
				Green-Dot	Unique	Blue-Dot
HODGDON						
H-322	H-4227	H-4895				
H-4198	H-4831					
				<b>Perforated Wafer</b>		
				DUPONT		
				700-X		PB
				<b>Flattened Ball</b>		
WINCHESTER-WESTERN				WINCHESTER-WESTERN		
WW-230	WW-540	WW-571	WW-680	WW-231	WW-296	WW-452AA
WW-748	WW-760	WW-785		WW-473AA	WW-630	
HODGDON						
H-414	BL-C	H-335		<b>Flake (Diamond Shaped)</b>		
<b>Ball</b>				S & W ALCAN		
HODGDON				AL-5	AL-7	AL-8
H-380	H-870					

double-base (DB) (Table 2)(9). A discussion of smokeless powder manufacture appears in the Encyclopedia of Explosives and Related Items, published by Picatinny Arsenal (10, 11, 12).

Gas chromatography (GC) has been used for the determination of plasticizers and stabilizers in composite double-base propellants and nitrated derivatives of glycerine (13, 14). A gas-liquid chromatographic method has also been developed for determining nitrate esters as well as stabilizers and plasticizers in a wide variety of nitrocellulose-base propellants (15). Proton magnetic resonance has been used by Picatinny Arsenal (16, 17, 18) for the identification of various explosive compounds.

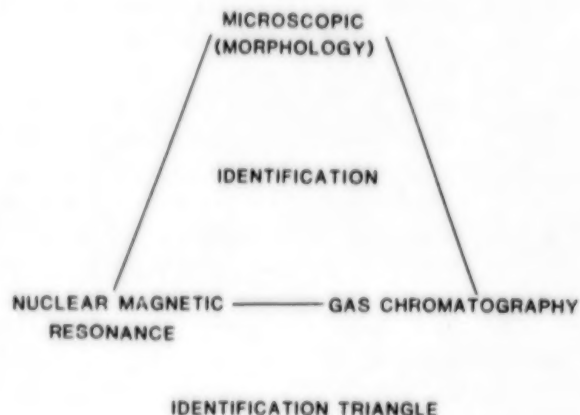


Figure 1. Identification Triangle.

Table 2. SINGLE-BASE AND DOUBLE-BASE PROPELLANTS.

Single-Base DUPONT			Double-Base DUPONT			
IMR-3031	IMR-4064	IMR-4198	700-X		800-X	
IMR-4227	IMR-4320	IMR-4350				
IMR-4831	IMR-495	SR-4756				
SR-7625	PB					
			WINCHESTER-WESTERN			
S & W ALCAN			WW-230	WW-231	WW-296	WW-452AA
			WW-473AA	WW-540	WW-571	WW-630
AL-5	AL-7	AL-8	WW-680	WW-748	WW-760	WW-785
	HODGDON		HERCULES			
H-322	H-4198	H-4227	Reloader 7	Bullseye		Green-Dot
H-4831	H-4895		2400	Unique		Red-Dot
			Blue-Dot			Herco
			HODGDON			
			BL-C	H-335		H-380
				H-414	H-870	

## EXPERIMENTAL

**Apparatus.** A commercial gas chromatograph, Hewlett-Packard 5880A with flame ionization detector (FID) was used in this investigation (Table 3). Column packings were obtained from Applied Science Laboratories. A Varian model Em 390 nuclear magnetic resonance (NMR) spectrometer was used to obtain the NMR-spectrum (Table 4).

Table 3. GAS CHROMATOGRAPHY CONDITIONS.

Columns:  
6 ft x 1/4 inch glass, 4 mm i.d.  
packed with 3% OV-17 on 100-120 mesh  
Gas Chrom Q  
Column temp 160-250°C  
Column temp program rate, 10°C/min.  
Detector temp 300°C  
Injection port temp 275°C  
Nitrogen flow, 60 cc/min.  
Sample size, 3 µl

Table 4. NUCLEAR MAGNETIC RESONANCE CONDITIONS.

Magnetic field strength	21,140 gauss
Field frequency	90 Mhz
RF Power	0.03 m G
Filter Time Constant	0.5 sec.
Reference	Tetramethylsilane (TMS)

**Procedure.** Deuteriochloroform (CDCl<sub>3</sub>) was selected as the NMR Solvent because of extraction problems with acetone. The smokeless powders, when dissolved in acetone, gelatinized and prevented the separation of the acetone from the solid

material. Approximately 500 mg of each smokeless powder was placed in 1.0 ml of CDCl<sub>3</sub>. The sample was allowed to stand in solution for at least 2 hours, and then half of the solvent was withdrawn and placed in an NMR tube.

Approximately 100 mg of each smokeless powder was dissolved in 2.0 ml of Methanol (MEOH) for examination by GC. A 3.0 µl sample was used for this purpose.

## RESULTS AND DISCUSSION

Smokeless powders can be initially categorized by their morphology. Visually, perforated wafers or discs, non-perforated wafers, ball, flattened ball, cylinder, or flake propellants can be readily distinguished. Next, determine whether they are single-base (SB) or double-base (DB). These two initial steps considerably narrow the areas of consideration for type/brand identification.

A PMR spectra is obtained to identify the manufacturer, and permit discrimination between similar products of the major U.S. manufacturers, namely, Dupont, Hercules, or Winchester-Western. At this point there is no absolute identification of the product type or brand name within the manufacturer's line. Additional information is required to distinguish company X's product A from product B. The GC profile of the methanol extract of the sample permits the observation of major and minor components. Combining the PMR and GC data allows discrimination of types within the product line of a single manufacturer.

When, from other information, the sample is suspected of being a Hodgdon powder, it must be examined very carefully. Hodgdon is not a manufacturer of smokeless powders. They purchase primarily from three basic sources: (1) ICI of Scotland, (2) Winchester-Western, and (3) U.S. Government surplus. From the spectra and chromatograms obtained in this work, Hodgdon powders were differentiated from each other as well as other manufacturers. Presently, it is not known what causes these differences, however, they may arise primarily from blending. Since the U.S. Government buys their powders from various manufacturers and if no further processing is performed, the particular composition may change with time. Therefore, future Hodgdon powders may not be readily differentiated from other commercial smokeless powders. Examples of typical PMR spectra and GC chromatograms are given in Figures 2 through 19.

As a result of this research project, it was determined that there were several areas that needed to

be considered for further work. The following is a listing of those areas of consideration. They have been placed in an order with the first being considered the most important. This order of importance may change.

1. Additional Domestic Propellants.
2. Propellants from other countries.
3. Sensitivity. What is the smallest sample size that can be analyzed?
4. Identification of the compounds in both the PMR Spectrum and GC Chromatograph.
5. Can differences be seen when smokeless propellants have been added to each other?
  - A. Same Brand
  - B. Different Brands
6. Differences within the same can of Propellant Powders.
7. Differences within the same batch.
8. Batch to Batch differences.
9. Relative aging of Propellants. Are there any differences over a given time period?
10. Detonated Smokeless Powders.

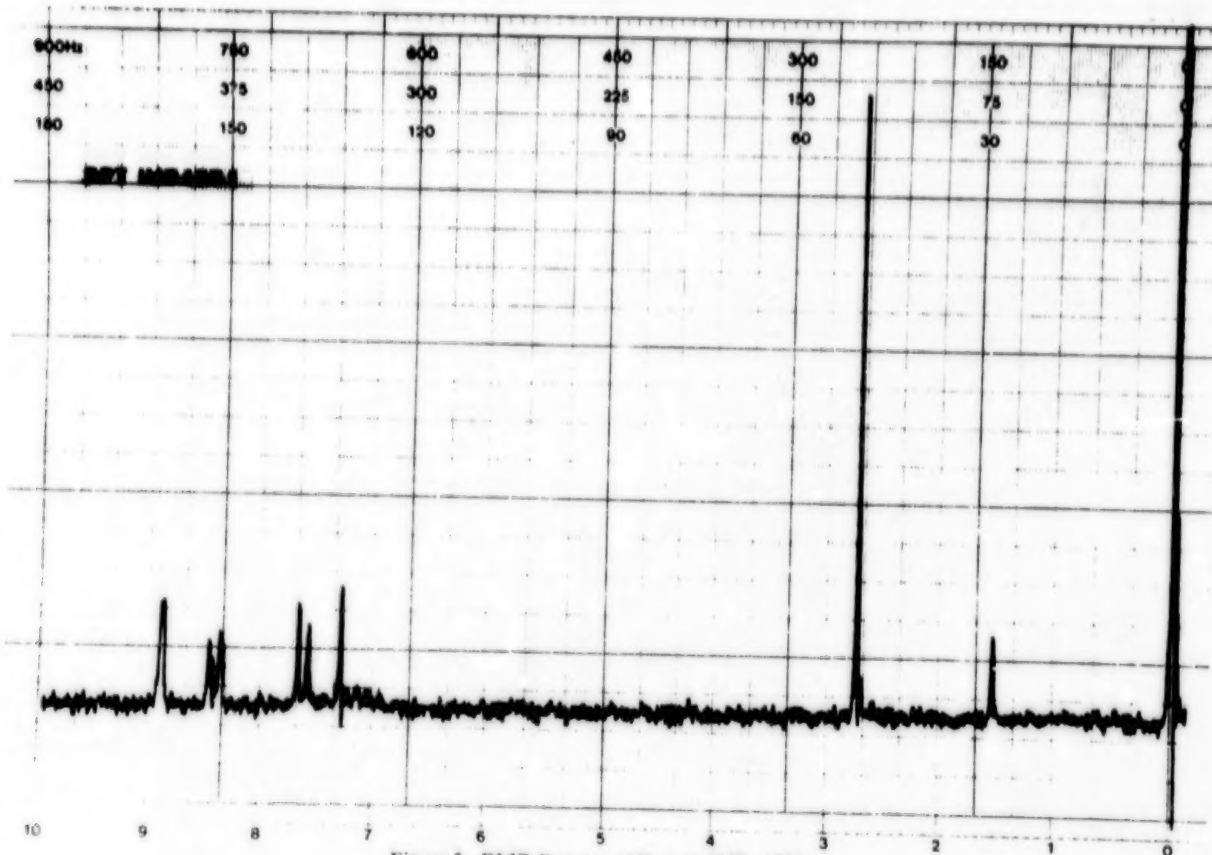


Figure 2. PMR Spectra of Dupont IMR-4831.

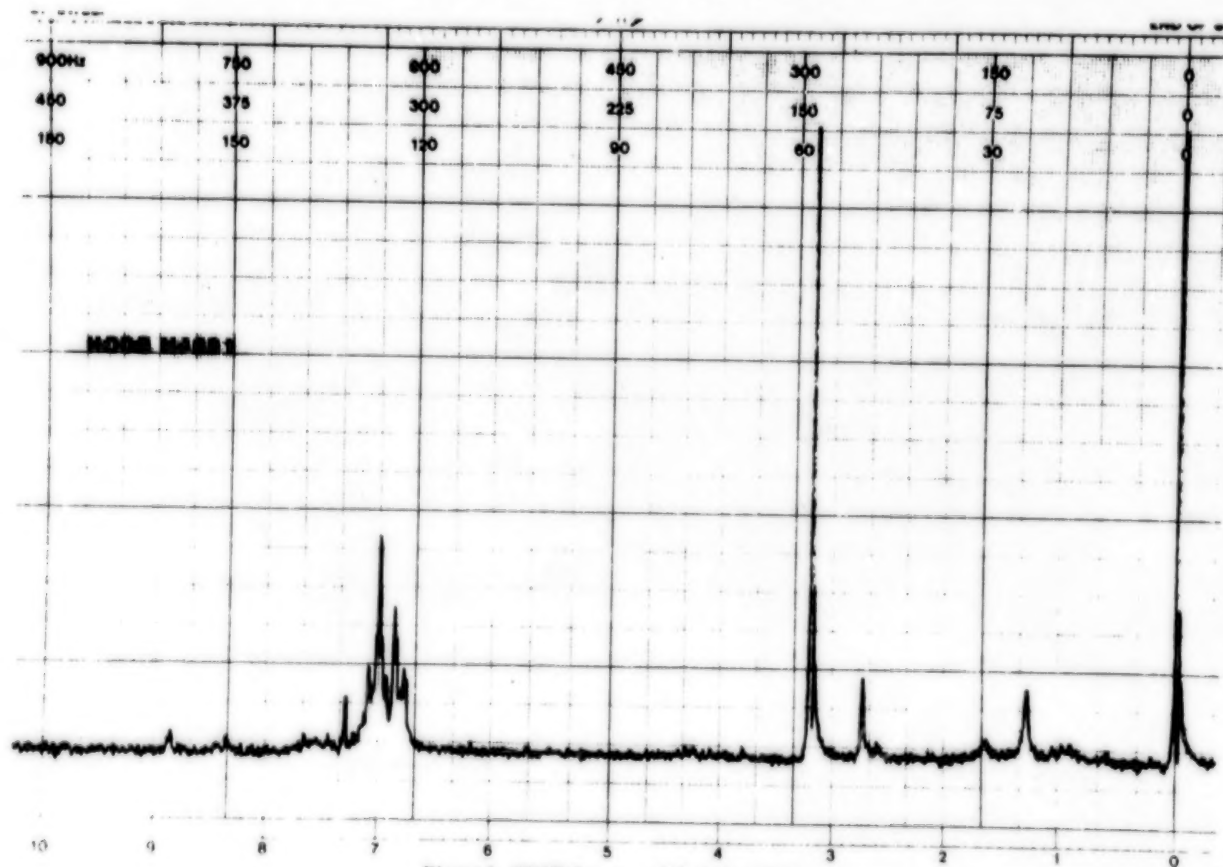


Figure 3. PMR Spectra of Hodgdon 4831.



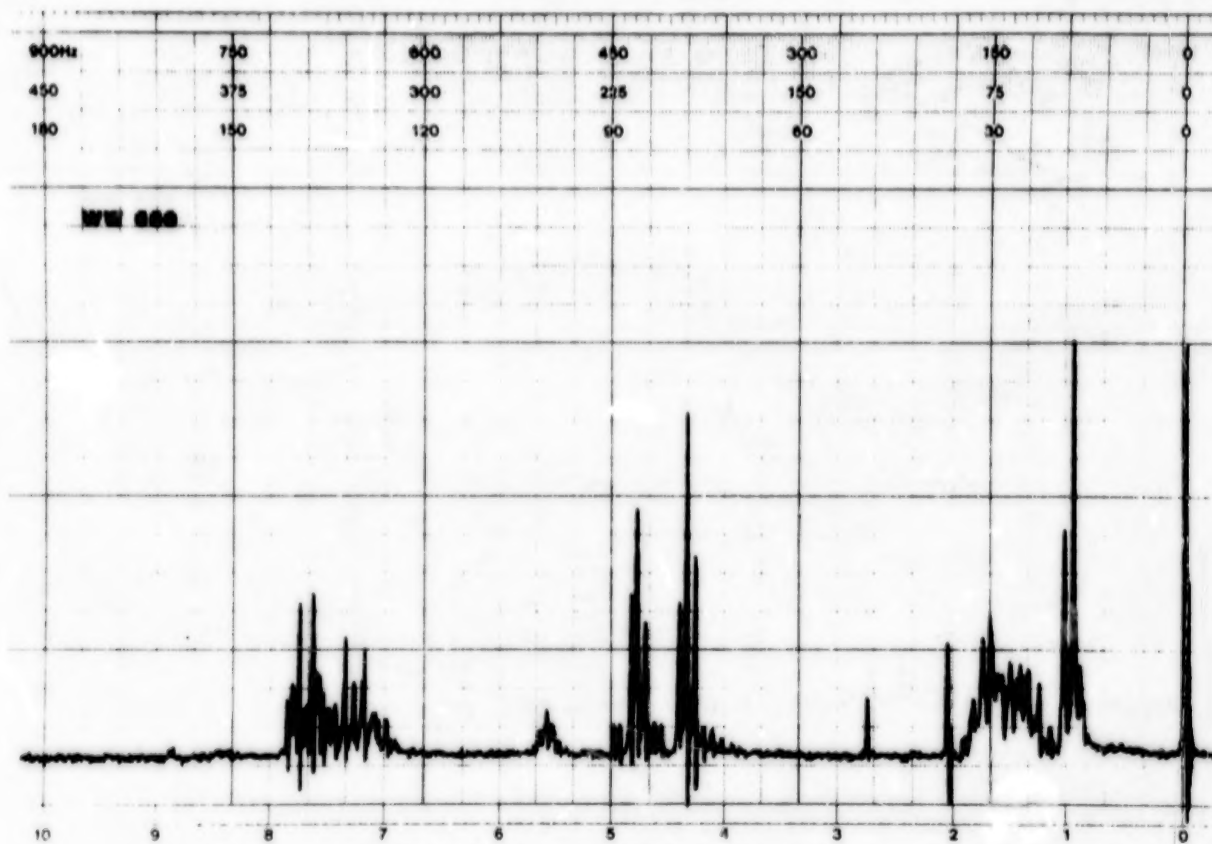


Figure 4. PMR Spectra of Winchester-Western 680.

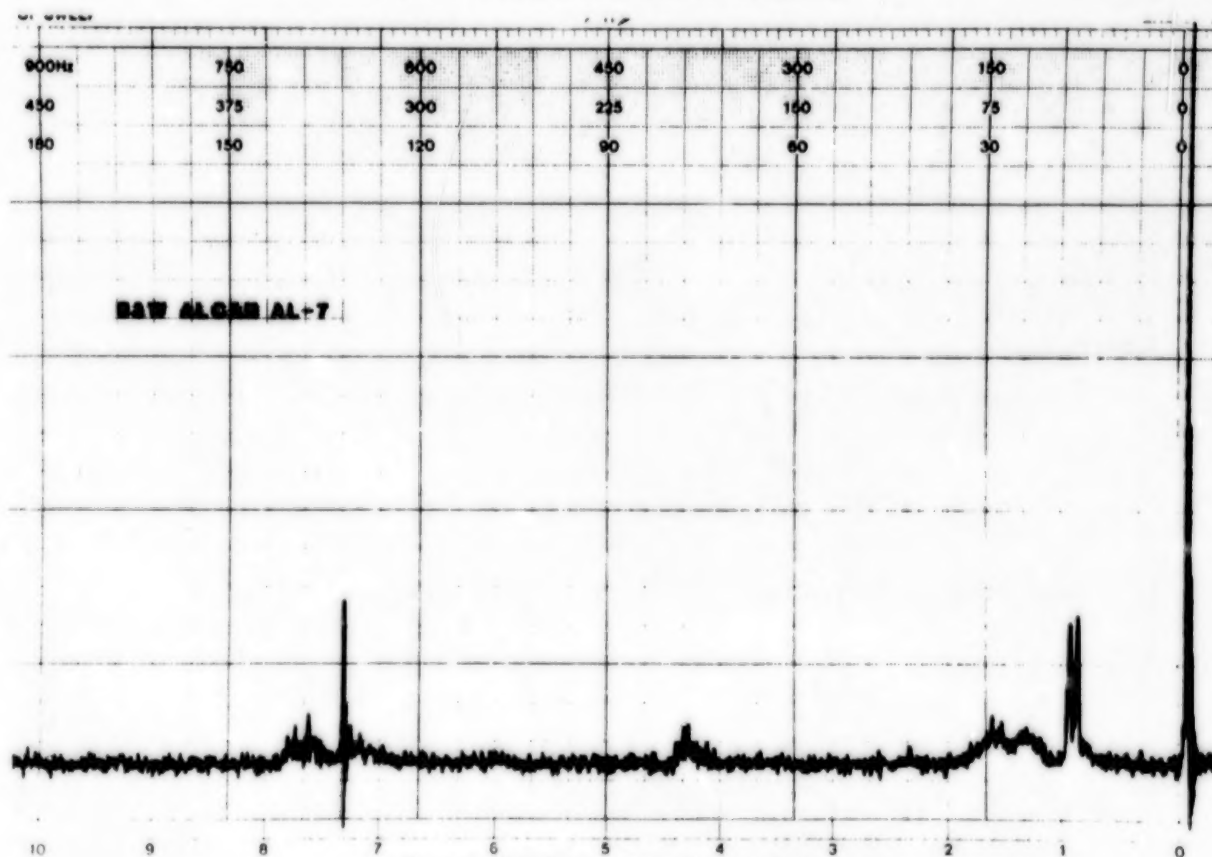
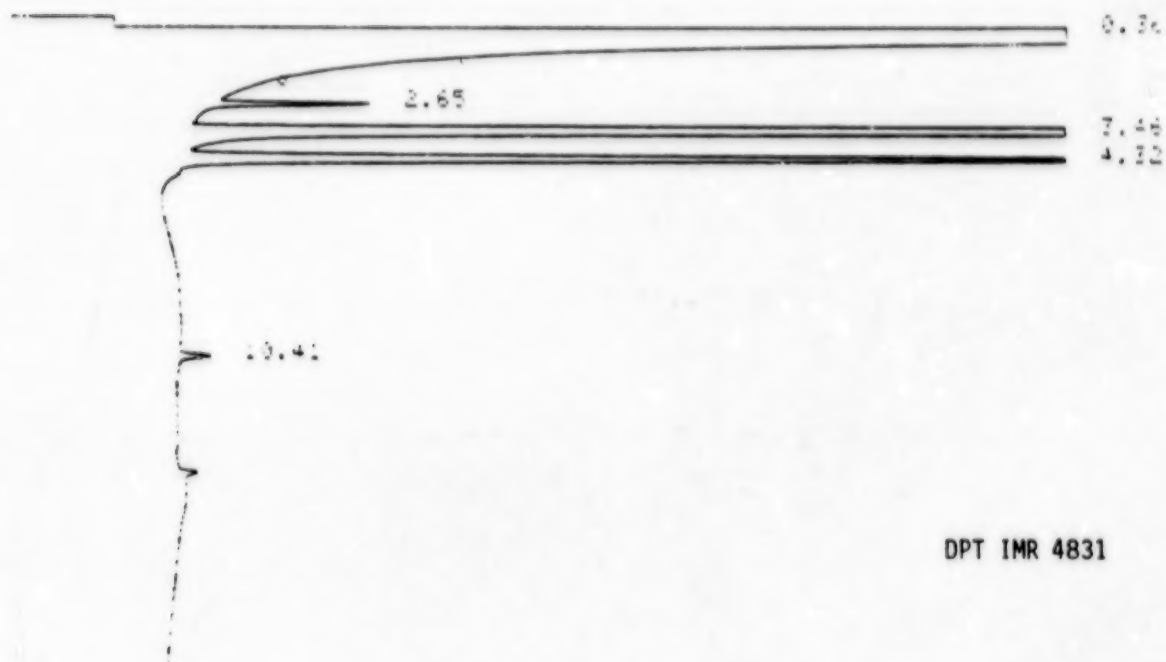


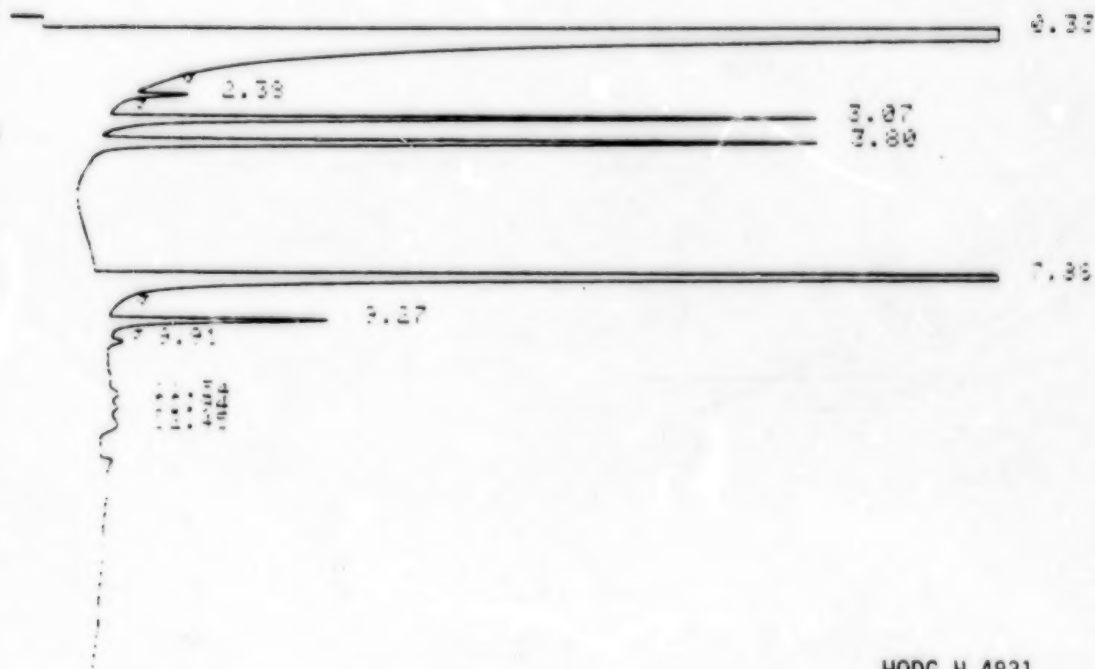
Figure 5. PMR Spectra of S & W Alcan AL-7.





DPT IMR 4831

Figure 6. Gas Chromatogram of Dupont IMR-4831.



HODG H 4831

Figure 7. Gas Chromatogram of Hodgdon H-4831.

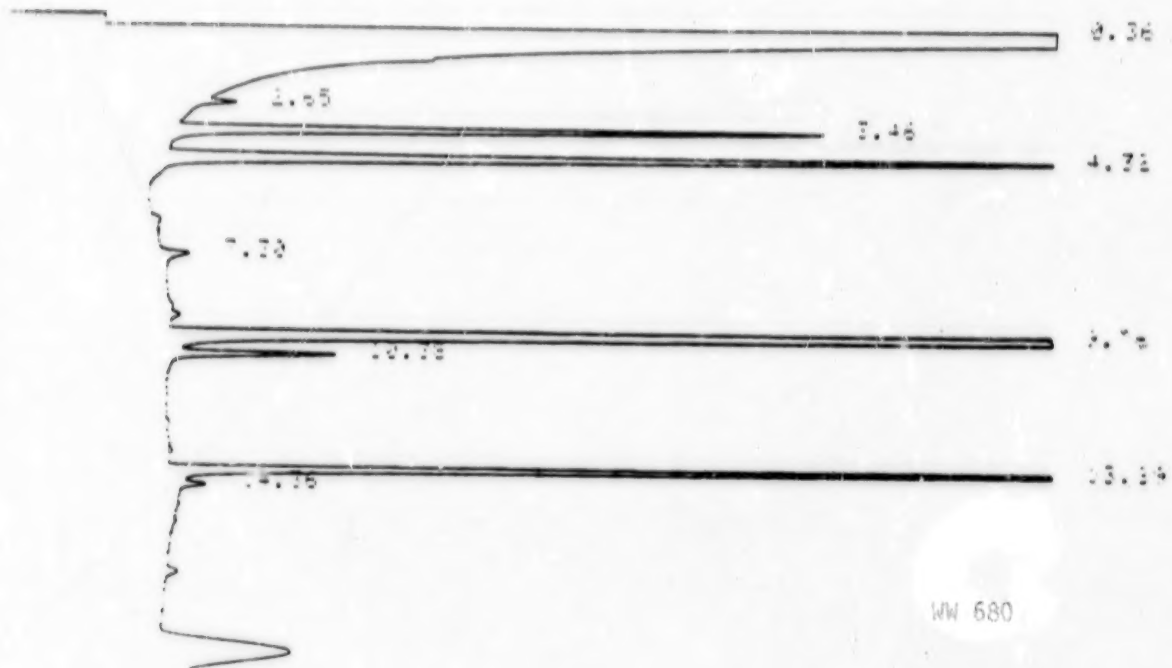


Figure 8. Gas Chromatogram of Winchester-Western 680.

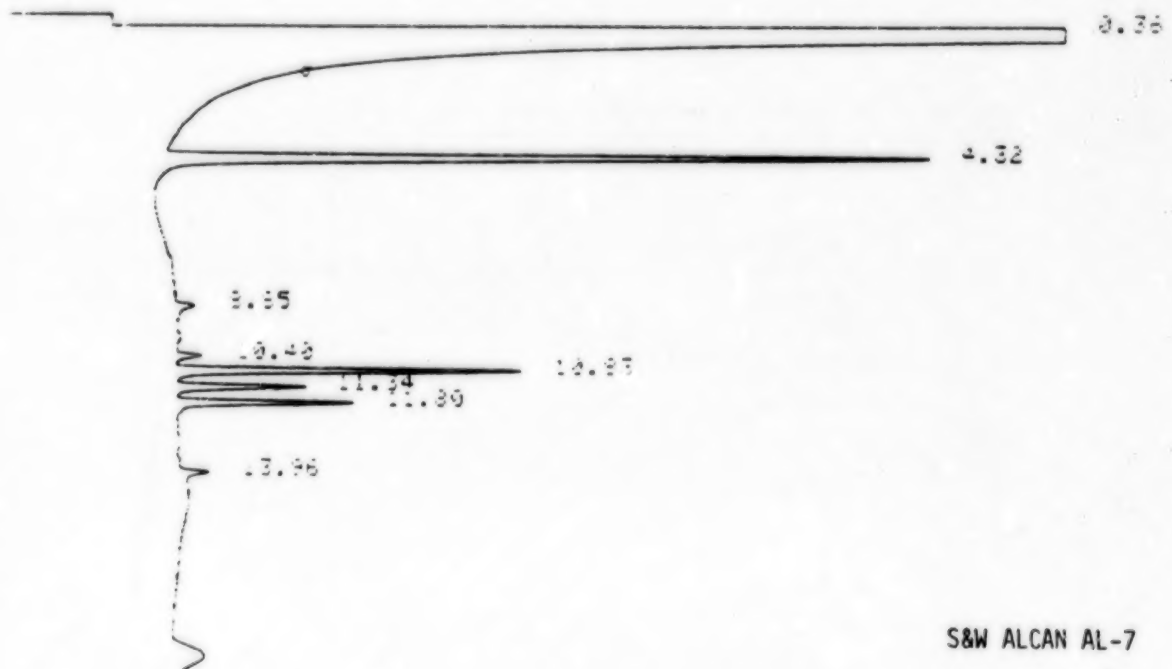


Figure 9. Gas Chromatogram of S & W Alcan AL-7.



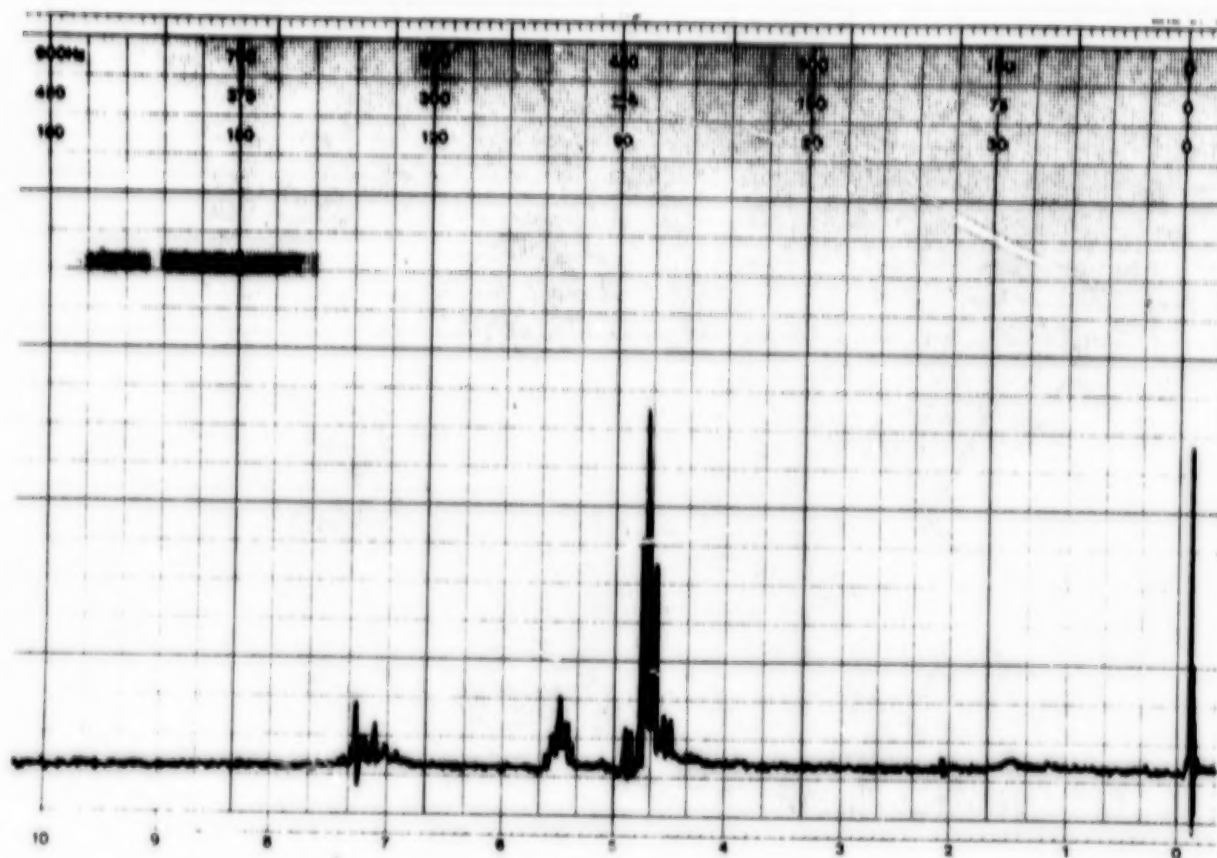


Figure 12. PMR Spectra of Hercules Green-dot.

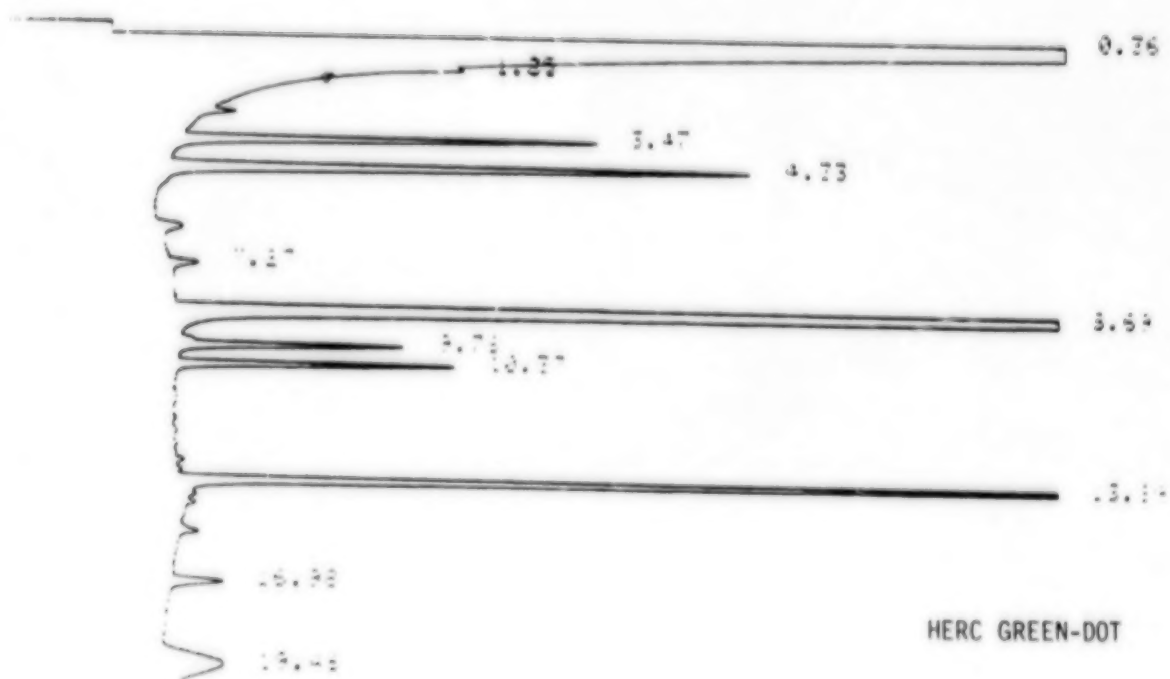


Figure 13. Gas Chromatogram of Hercules Green-dot.

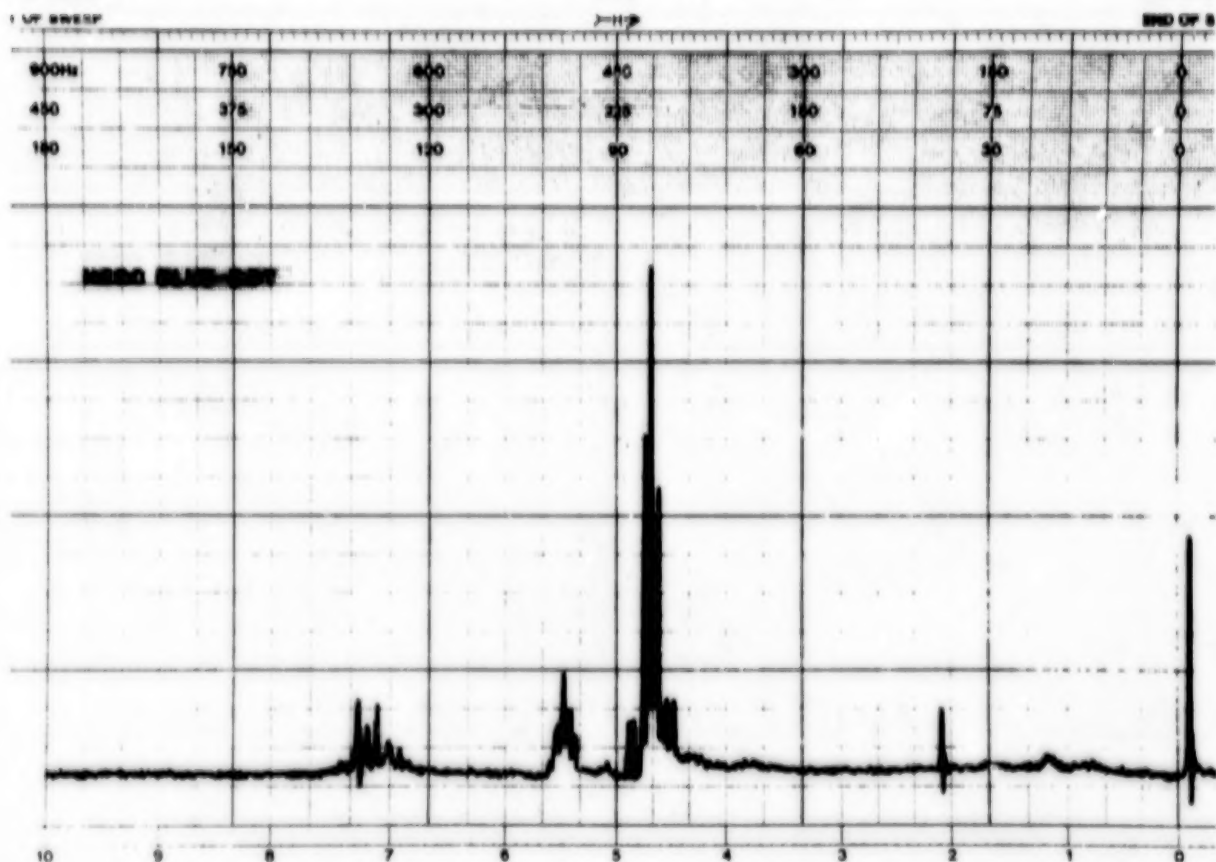


Figure 14. PMR Spectra of Hercules Blue-dot.

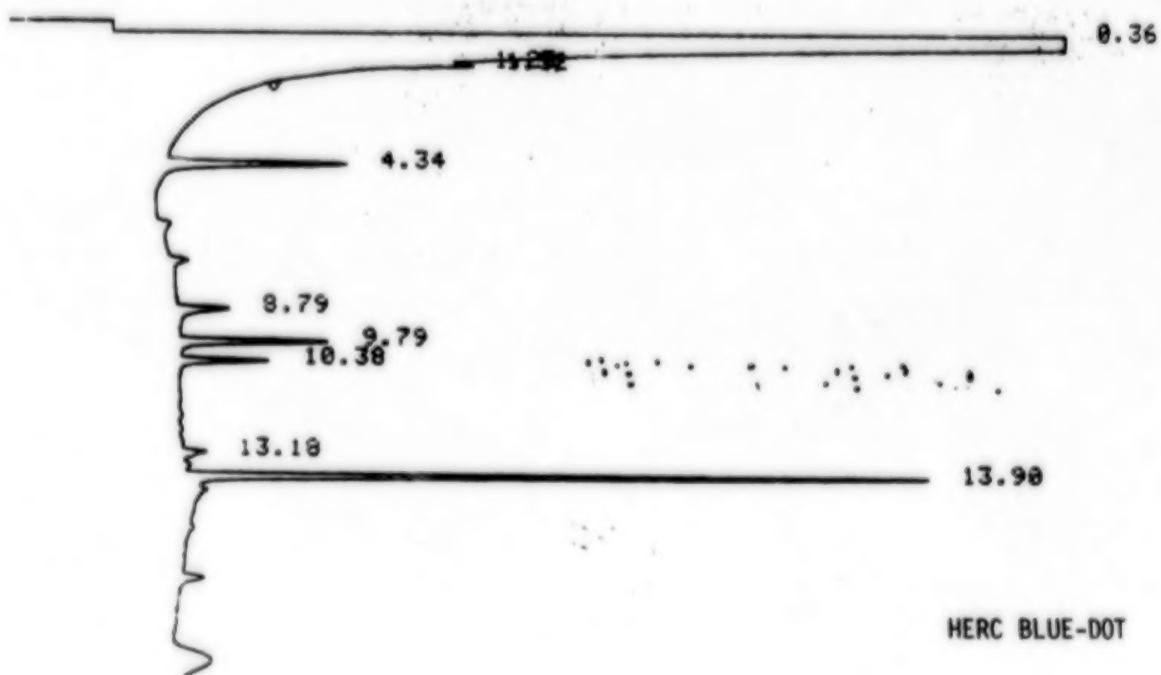


Figure 15. Gas Chromatogram of Hercules Blue-dot.

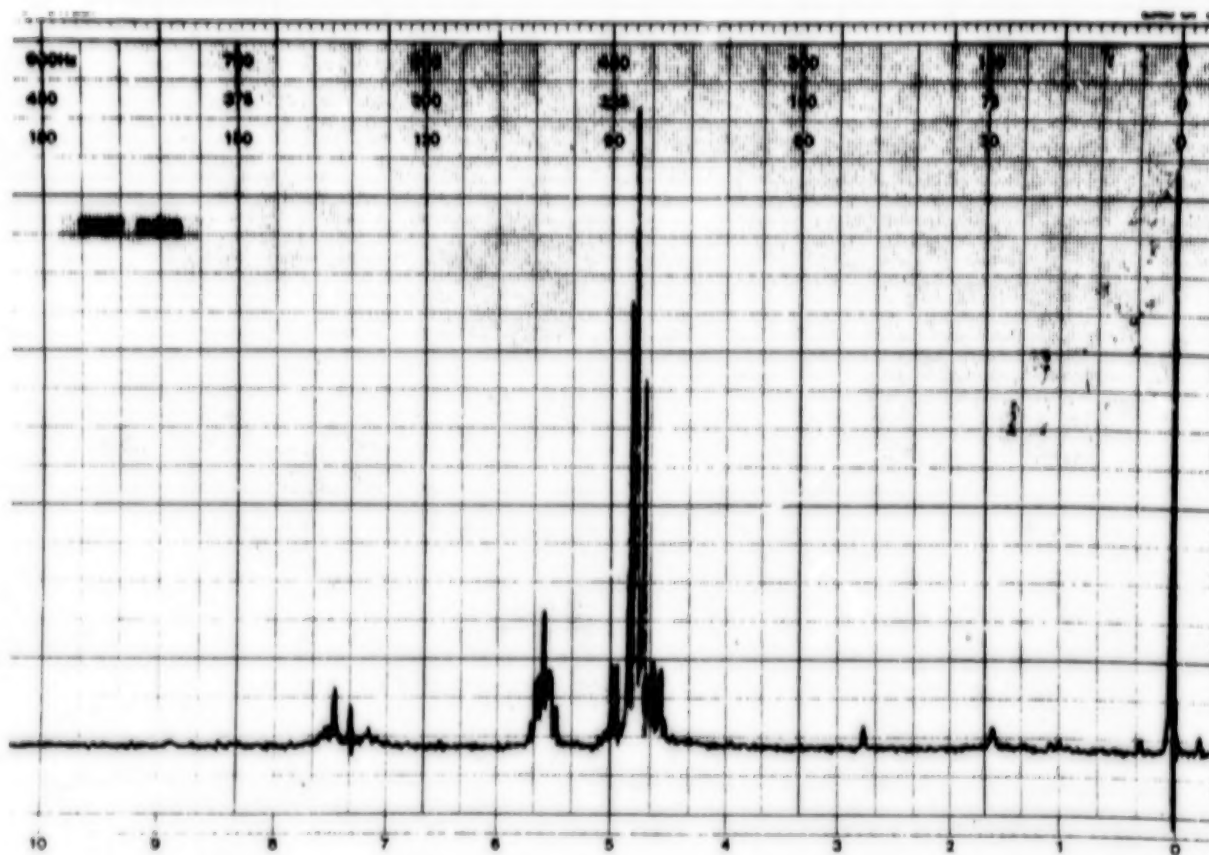


Figure 16. PMR Spectra of Winchester-Western 230.

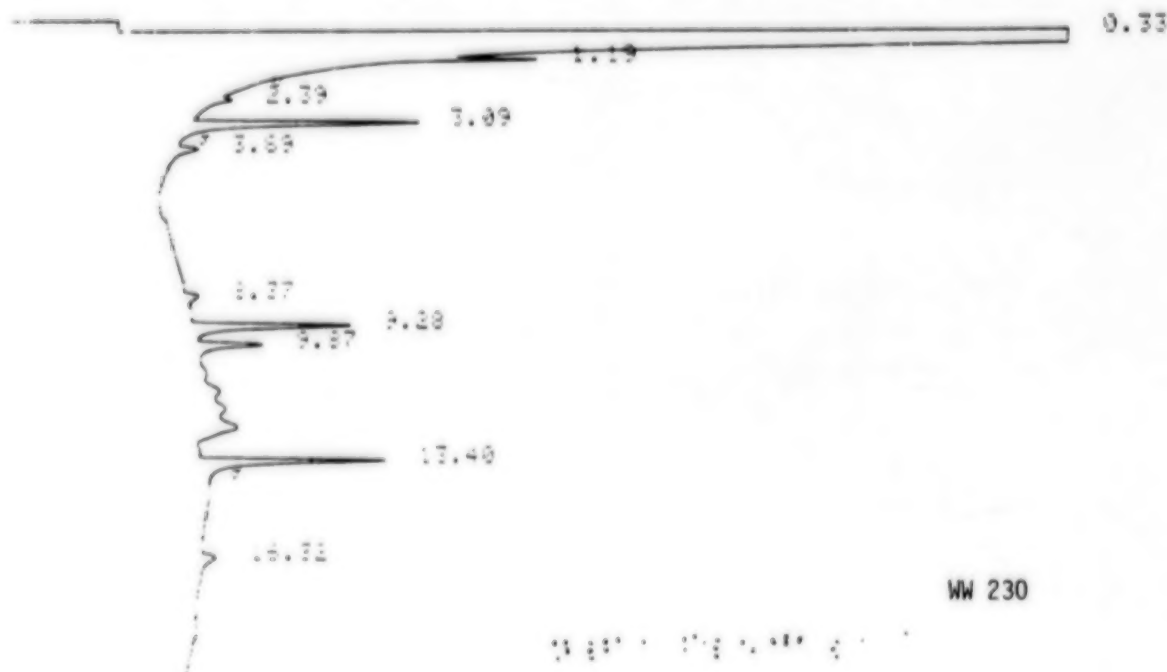


Figure 17. Gas Chromatogram of Winchester-Western 230.



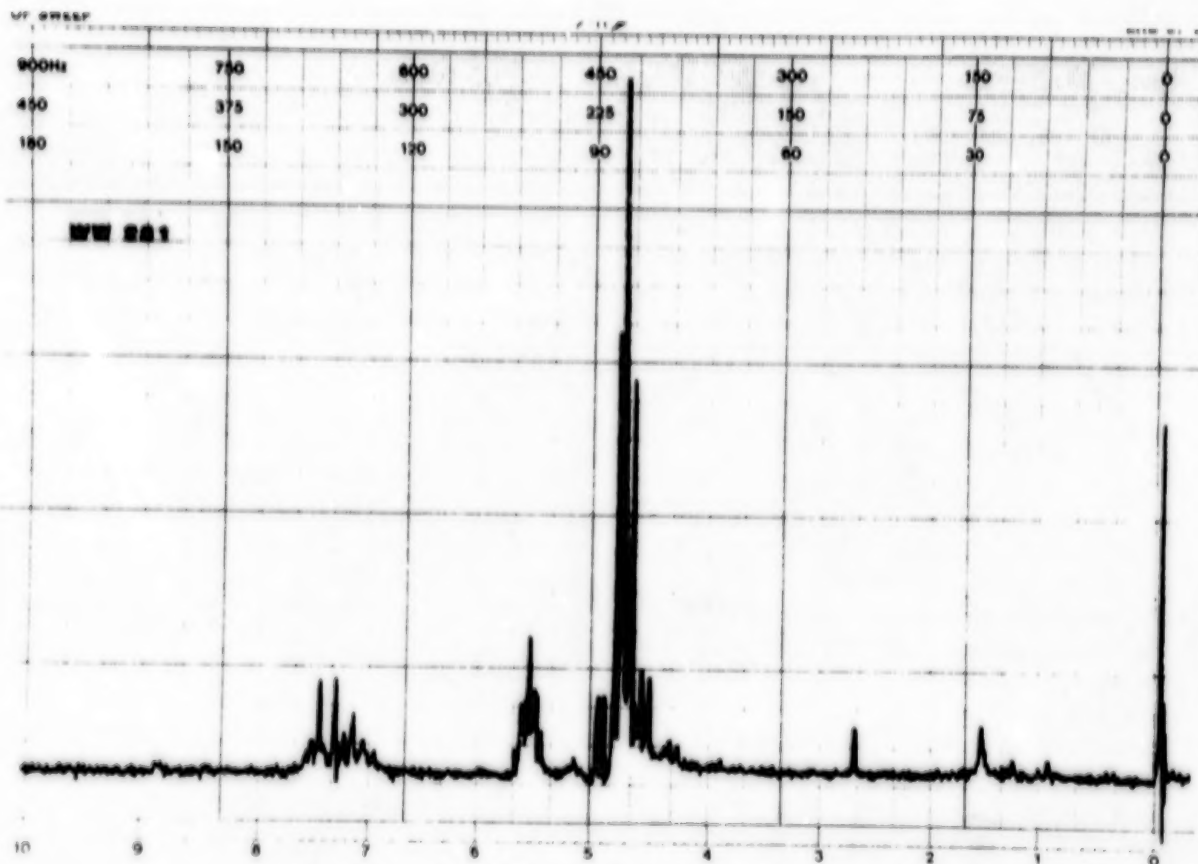


Figure 18. PMR Spectra of Winchester-Western 231.

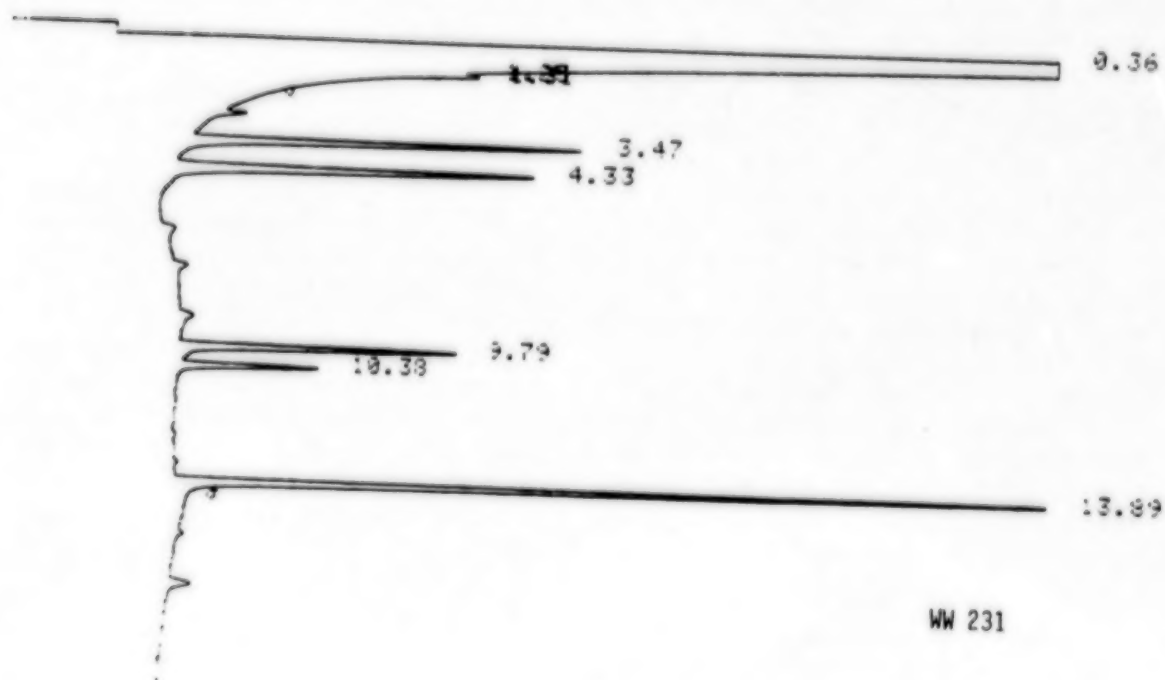


Figure 19. Gas Chromatogram of Winchester-Western 231.

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# THE USE OF MULTIPLE DETECTION IN THE GAS CHROMATOGRAPHIC ANALYSIS OF ORGANIC NITRO COMPOUNDS AND EXPLOSIVES (GC-ECD/PID)

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**Abstract.** The trace organic analysis for nitro derivatives and explosives has traditionally been hampered in gas chromatography by a lack of suitably selective and sensitive detectors. Except for the mass spectrometer, and perhaps the Thermal Energy Analyzer, most other GC detectors are not suitably selective for nitro compounds to provide unambiguous identification of trace amounts in complex sample matrices. In recent years, numerous workers have applied a combination of detectors, in series or parallel, for improved compound identifications. We have now utilized a parallel arrangement of electron capture detection (ECD) and photoionization detection (PID), together with certain Permabond GC packing materials, for the improved resolution and specific identification (speciation) of numerous organic/nitro compounds and explosives. The combination of GC-ECD/PID for nitro derivatives provides relative response factors vs a common internal standard, as well as ratios of ECD/PID relative response factors that are often unique for individual nitro compounds. We have now applied these analytical methods to a wide variety of nitro derivatives, including: mono-nitro toluenes; dinitrotoluenes, dinitrobenzenes, nitro aliphatics, nitro-PAHs, polycyclic aromatic hydrocarbons (PAHs), and various explosive compounds. Separations of mixtures of the aromatic nitro derivatives, PAHs, nitro-PAHs, or explosives, were obtained using glass packed columns of Permabond Methyl Silicone, Permabond PEG 20M, and/or Permabond PAH packings. In most instances, temperature programmed separations were interfaced with fixed ratio splitting of the GC effluent to the ECD and PID detectors. The combination of ECD and PID provides for vastly different response factors in comparing the PAHs and nitro-PAHs, so that the resultant normalized relative response factors for the ratio of ECD/PID become vastly different on an absolute scale. Thus, in certain cases, PAHs and their nitro-PAH derivatives can exhibit 3-7 orders of magnitude differences in their relative response factors for ECD/PID ratios.

The use of combined ECD/PID ratios and relative response factors in GC analyses for organic nitro compounds and related explosives provides a unique method of utilizing relatively available detectors for improved analyte identification and specificity at little added overall cost. These methods are directly applicable to environmental samples containing trace amounts of nitro derivatives and/or explosives. Gas chromatography-multiple detection is a very viable and valid method

for the trace analysis of these types of compounds. (This work was supported, in part, by an NIH Biomedical Research Support Grant No. RR07143 to Northeastern University, Department of Health and Human Services.)

### SUMMARY

Combined detectors in gas chromatography (GC), such as electron capture detection (ECD) and photoionization detection (PID) have now been utilized for improved qualitative identification of a wide variety of organic nitro compounds. GC retention times together with relative response factors and ratios of ECD/PID response factors are reported for this class of derivatives. Minimum limits of detection on ECD and PID, relative response factors, and ratios of relative response factors (RRF/RRF) are derived from mixtures of organic nitro compounds separated *via* GC with temperature programming. A new type of GC packing material, the covalently bonded Perma-bond supports, are utilized for most of these studies with combined ECD/PID detection in GC. Organic nitro compounds are of considerable interest because they are widely distributed as environmental pollutants and toxicants, as well as being found in explosives, veterinary products, pharmaceuticals, perfumes, cosmetics, propellants, industrial raw materials, and finished consumer products.

### INTRODUCTION

Organic nitro derivatives are a class of compounds that are of current analytical and toxicological interest due to many reasons. A large number of aliphatic and aromatic nitro compounds, such as those in Figures 1 and 2, have to different degrees, already been found in various environmental, industrial, biological, and chemical samples. At times, such compounds are formed within such samples from suitable precursors, and at times, they are initially present as contaminants from other sources [Scheutle *et al.* (1982), Pitts *et al.* (1979, 1978), Rosenkranz *et al.* (1980), Lofroth *et al.* (1980), Rosseel and Bogaert (1979), Yap *et al.* (1978), Krull and Camp (1980)]. It has also become of considerable concern that a very large number of nitro compounds, especially the poly-aromatic derivatives, display varying degrees of mutagenicity and/or carcinogenicity [Cohen *et al.* (1976), Wang *et al.* (1975), Wang *et al.* (1978), Won *et al.* (1976), Griswold *et al.* (1968), Pitts *et al.* (1977), Khudoley *et al.* (1981), Goodall and Kennedy (1976), Whong *et al.* (1980)]. Many nitro compounds are used as drugs, veterinary prod-

ucts, cosmetic ingredients, perfumes and fragrances, explosives and propellants, agricultural chemicals, industrial raw materials and intermediates, bactericides, and other consumer/industrial products. Because of their wide chemical diversity and widespread distribution *via* consumer and industrial products, as well as the fact that many are formed environmentally, it has become obvious that many nitro compounds have become widespread environmental pollutants and/or contaminants. There has therefore developed an intense interest in the development of trace methods of analysis and speciation for various nitro derivatives, including the use of gas chromatography (GC) with a variety of detectors, high performance liquid chromatography (HPLC) with assorted detectors, as well as direct analysis *via* mass spectrometry (MS) and related instrumental techniques [Demko (1979), Mourey and Siggia (1979), Takagi *et al.* (1981), Ramdahl *et al.* (1982), Langhorst (1981)]. In the past, most trace analyses for various nitro compounds present in complex sample matrices, involved the use of GC with a variety of selective and/or general detectors, such as flame ionization detection (FID), electron capture detection (ECD), alkali flame ionization detection (AFID), Thermal Energy Analysis (TEA), Coulson electrolytic conductivity detection (CECD), and others. Within the past few years, a very large number of HPLC based analyses for nitro compounds have been described, making use of electrochemical detection (EC), electron capture detection (ECD), photoconductivity detection (PCD), Thermal Energy Analysis (TEA), and others [Krull and Camp (1980), Krull (1983), Krull *et al.* (1981), Jacobs and Kissinger (1982), Bratin *et al.* (1981)].

Most trace analyses for organic nitro compounds still rely on GC-detector methods, in part because of the lower detection limits possible and the general widespread availability of the instrumentation required. Of late, there has been a distinct interest in the application of photoionization detection (PID) for a wide variety of trace organic analyses. At the same time, there is considerable interest in combining the PID with other selective and/or general GC detectors for improved analyte identification in trace analysis [Driscoll *et al.* (1982), Driscoll *et al.* (1980), Jaramillo and



Driscoll (1979), Driscoll *et al.* (1978a), Driscoll *et al.* (1978b), McKinley *et al.* (1982), Conron *et al.* (1982), Langhorst and Nestrick (1979)]. The use of more than one detector response per analyte of interest has recently gained widespread popularity and acceptance as a valid analytical method for improving the qualitative identification of individual GC analytes [Gagliardi *et al.* (1981), Parliment (1982), McCarthy *et al.* (1981), Bachmann *et al.* (1977), Poy (1979), Bjorseth and Eklund (1979), Cox and Earp (1982)]. In most applications, the combination of a general and selective or selective and selective detector for organic nitro compounds should provide more compound specificity and identification than the use of two detectors that both respond to about the same extent with such materials. Thus, the use of FID and ECD for nitro compounds would not be expected to provide any unusual degree of analyte specificity, because most/all aliphatic or aromatic nitro compounds would provide about the same degree of response on both FID, or ECD. On the other hand, a combination of FID with PID, or ECD with PID, or all three detectors simultaneously, should provide an unusual degree of compound identification and specificity. This assumes, of course, that the PID will indeed demonstrate more selectivity for aliphatic vs aromatic nitro derivatives than either the FID or ECD. This assumption has been supported by the earlier work of Driscoll *et al.* (1978b). With regard to the application of the PID for nitro derivatives in general, this has been described for a very limited number of variety of such compounds by Langhorst (1981). This paper described the PID relative responses vs benzene for nitrobenzene, 2,4-dinitrotoluene, 4-nitrophenol, and 2,4-dinitrophenol, but there was no mention of any aliphatic nitro derivatives.

We describe here the simultaneous application of both ECD and PID for a large number of aliphatic and aromatic nitro derivatives, including: nitropentane, nitrocyclohexane, o-, m-, and p-nitrotoluene, 2,3-, 2,4-, 2,6-, and 3,4-dinitrotoluene, o-, m-, and p-dinitrobenzene, polycyclic aromatic hydrocarbons and their mono-nitro derivatives (Figures 1 and 2). PAHs and nitro-PAHs are of considerable interest as environmental air and water pollutants, and because of their demonstrated carcinogenicity and/or mutagenicity in mammalian systems. All of these GC-ECD/PID analyses have been performed with either Ultrabond 20M, Permabond Methyl Silicone, and/or Permabond PEG 20M packing

materials in glass packed columns. Permabond packing materials have recently gained widespread attention because of their very light loading, covalent attachment of the liquid (organic) phase to the solid, inert support, and their general high temperature stability [Langhorst (1981), Langhorst and Nestrick (1979)]. We describe here the GC separation conditions utilized, detector operating parameters, retention times and resolution factors, minimum limits of detection *via* ECD/PID, linearity ranges of response, normalized response factors on various detectors, and related, appropriate analytical parameters of interest for these nitro derivatives. All of this work has, thus far, involved the use of commercially available chemical standards, but the final analytical and detection methods and results should be directly applicable to real world samples for these and other nitro derivatives. It is the intention of this work that such methods will indeed be eventually applied in other laboratories to practical environmental, industrial, biological, and toxicological sample matrices of interest to workers in such fields.

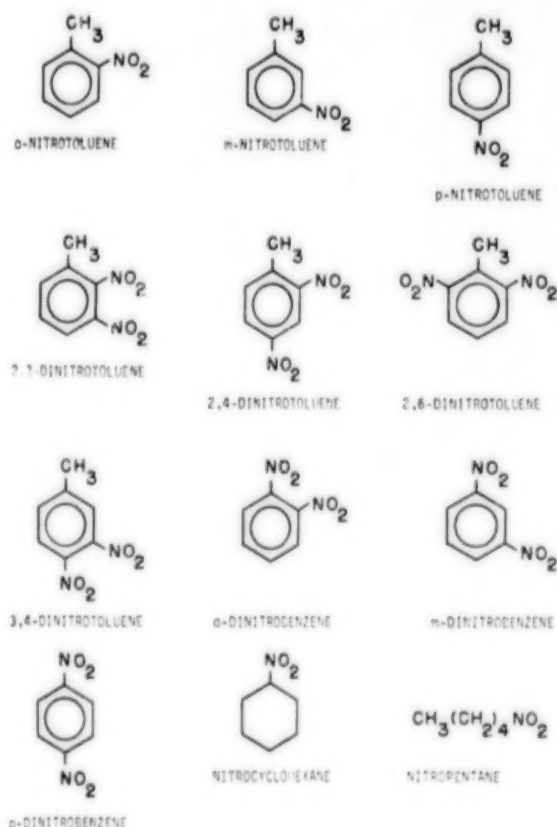


Figure 1. Aliphatic and aromatic nitro derivatives studied *via* GC-ECD/PID with Permabond column packings.

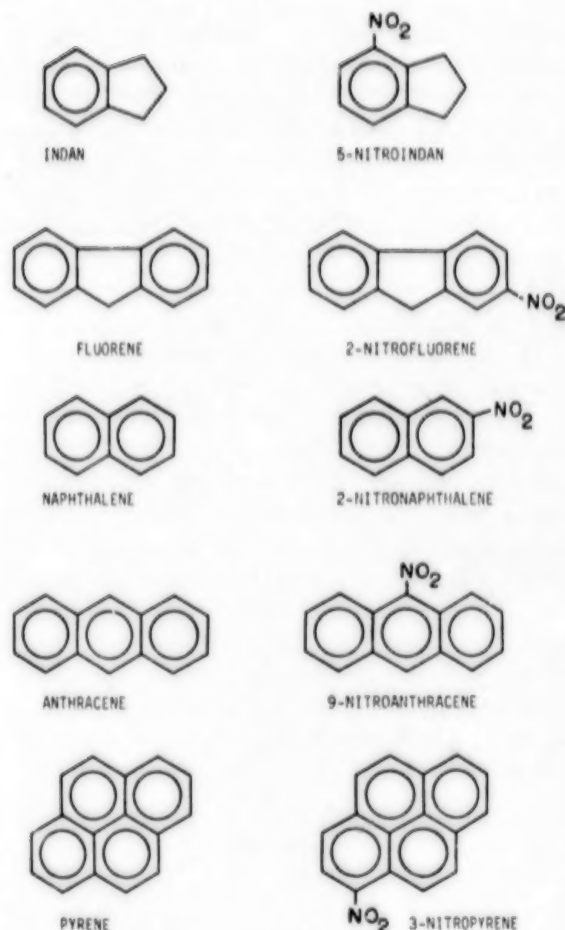


Figure 2. Polycyclic aromatic hydrocarbons (PAHs) and nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) studied via GC-ECD/PID with Permabond column packings.

## EXPERIMENTAL

### Equipment

These results were obtained using a Varian Model 3700 gas chromatograph (Varian Associates, Inc., Palo Alto, Calif.), equipped with conventional Varian FID and ECD detectors. A separate PID unit was mounted external to the main GC oven, on top of the GC itself, with external heating tape applied to the interface, in order to prevent any condensation of the GC effluents after their exit from the column oven. The PID was obtained from HNU Systems, Inc., Model No. PI-51-01 (HNU Systems, Inc., Newton, Mass.). For dual detection in parallel, *viz.*, ECD/PID, it was necessary to construct a special, glass-lined, metal tee splitter using  $\frac{1}{8}$ -in x 0.5-mm i.d. glass-lined stainless steel tubing (Scientific Glass Engineering, Inc., Austin, Texas). Additional parts for this all glass-lined interface between the end of the GC column and the two detectors in-

clude drilled through Swagelok reducing union,  $\frac{1}{8}$ -in x  $\frac{1}{8}$ -in, (Cambridge Valve & Fitting, Inc., Billerica, Mass.), and Varian detector inlets (Varian Corp.). A Weller Mini-Shop variable speed cutter with a diamond cutting wheel (Jensen Tools, Tempe, Arizona) was used to cut the glass-lined metal tubing. This fixed ratio splitter was monitored before, during, and after various days' analyses, to ensure that the actual eluent split to each detector was reproducible and well defined. Temperature programming does not change the eluent split ratio using this type of a fixed ratio GC splitter.

For those studies involving only nitropentane, nitrocyclohexane, *o*-nitro-toluene, and 2,6-dinitrotoluene in the analyte mixture, a GC column packing of Ultrabond 20M (RFR Corp., Hope, R.I.) was used, in a packed glass column, 6-ft x 2.0-mm i.d. All of the aromatic nitro derivatives, PAHs, and nitro-PAHs were eventually analyzed on two separate GC columns with slightly different temperature programming conditions. The first such column was a glass packed column 6-ft x 2.0-mm i.d., of Permabond Methyl Silicone (HNU Systems, Inc.). The second GC column in this series was a glass packed column 6-ft x 2.0-mm i.d., of Permabond PEG 20M (HNU Systems, Inc.). Specific GC separation conditions for each of these columns are indicated below (Results and Discussion). The support gases used for the GC carrier gas and detector support gases (FID) were obtained from Matheson Gas Co. (East Rutherford, N.J.). All GC-detector chromatograms were recorded on a Linear dual pen recorder (Linear Instruments Corp., Irvine, Calif.) at a chart speed of 1 cm/min and an output of 1 mV.

### Reagents and Solvents

Individual nitro compounds, PAHs, or nitro-PAHs, were obtained from a variety of commercial sources, including: Pfaltz & Bauer, Inc. (Stamford, Conn.), Aldrich Chemical Co. (Milwaukee, Wisc.), Chem Service (West Chester, Penna.), MCB Chemicals, Inc. (Medford, Mass.), or Fisher Scientific, Inc. (Fair Lawn, N.J.). All of the solvents used to prepare the standard solutions for GC analyses were HPLC grade, distilled-in-glass, and were obtained from commercial suppliers, such as: J. T. Baker Chemical Co. (Phillipsburg, N.J.) or MCP Omnisolv (Doe & Ingalls, Inc. (Medford, Mass.)). Chemicals and solvents were not purified further, but were used directly as received from the supplier.



## Methods

Individual stock solutions of each nitro derivative or mixtures of nitro compounds, PAHs, or nitro-PAHs were prepared in volumetric flasks by carefully weighing or measuring out an initial amount of each standard. The solvents used to dissolve such chemical standards were chosen so that they would be compatible with the particular GC detectors being used. In most cases, acetone alone or a 1:1 (v/v) mixture of hexane:acetone was satisfactory for such standard solutions. Solutions once prepared were kept in the dark in the refrigerator, and if a question arose with regard to changes in concentration levels, then fresh standard solutions were prepared the same day as the analytical studies involved. All standard solutions were prepared with an internal standard, *o*-nitrotoluene, added at the same time as the compounds of interest. Injections onto the GC were made with a Hamilton Model No. 701N syringe (Hamilton Company, Reno, Nevada), and these were generally less than 2  $\mu$ l injections. Solvent blanks were always injected before and after the standard solutions of analytes, to ensure that any peaks being observed were not derived from the solvent itself or any impurities therein. All injections of standards and solvent blanks were performed at least in duplicate, under identical GC-detector operating conditions.

The nitroaromatics and nitro-PAHs were converted to their expected amino derivatives using a tin/HCL reduction method. This consisted of adding 1g of the nitro compound to 2g of granulated tin in a small flask. The flask was connected to a reflux condenser, and 20 ml of 10% HCL was added in small portions, with vigorous shaking after each addition. The mixture was then warmed on a steam bath for 10 mins, the solution was decanted while hot, and sufficient 40% sodium hydroxide solution was added to dissolve the tin hydroxide. The solution was then extracted several times with 10ml portions of ethyl ether. The ether extracts were then combined, dried over anhydrous sodium sulfate, filtered from the drying agent, and this final solution was either directly injected onto the GC or first diluted with additional ether before injection.

## RESULTS AND DISCUSSION

All of the analytical results presented here have been obtained using packed glass columns, mostly with Permabond type packing materials, and in most instances using temperature programming.

Capillary columns have always been an alternative approach, but this would have required the use of somewhat modified detectors, in order to fully utilize the efficiencies inherent within capillary columns. We have not found it necessary to utilize capillary columns for these studies, since improved analyte specificity has been realized with conventional packed columns together with the different selectivities inherent in ECD and PID detection methods. Combined detector responses, normalized relative response factors (RRFs), and ratios of such relative response factors (ECD/PID), have provided greatly improved selectivity over single detector methods in conventional GC. For unusually complex sample mixtures, capillary column resolutions may prove a necessity, but this would then require suitable modifications in the dimensions of the conventional GC detectors employed.

In all of the PID analyses, a 10.2 eV lamp has been used, in part because of its greater light intensity at this power level. Since other, higher and lower, eV lamps are commercially available, it should be possible in future work to obtain additional selectivity differences for these same nitro derivatives or PAHs. Such data, together with the same ECD responses described below, would then provide additional analyte identification and selectivity. Clearly, the ability to vary the power (energy) level of the commercial PID unit, together with conventional ECD applications, offers the analyst an unusual degree of compound/analyte selectivity and specificity.

We have compared the selectivity possible for equi-molar amounts of four typical organic nitro compounds, *viz.*, nitropentane, nitrocyclohexane, *o*-nitrotoluene, and 2,6,-dinitrotoluene, Figure 1, using FID, ECD, and PID. Figure 3 illustrates the GC-FID/PID chromatograms for these four standards, with the amounts of each reaching the detectors as indicated. Specific GC-detector conditions are indicated in Figure 3 and above (Experimental). As expected, the FID responses are approximately equal for equi-molar amounts of organic nitro compounds, on a general type detector. However, the PID responses are vastly different, especially when comparing aliphatic nitros vs aromatic nitro compounds. Even at the low  $\mu$ g/compound levels injected here, neither of the aliphatic nitro derivatives appear on the PID. The differences in sensitivities for organic nitro compounds must be due to inherent differences in the ionization potentials of these compounds, since

this is the physical basis for the selectivities possible with the PID. The absolute amounts of each compound reaching the PID are in the 5–10 $\mu$ g range. The GC-ECD analysis for these same four organic nitro compounds showed, as expected, approximately equal responses for the mono-nitro materials for equi-molar amounts reaching the ECD, and about a doubling of the response for the 2,6-dinitrotoluene isomer. Thus, of all three detectors initially studied here, only the PID shows a high degree of selectivity for aliphatic and aromatic nitro derivatives.

With regard to the minimum detection limits (MDLs) for these same four nitro materials, and thus indirectly the relative response factors (RRFs), this data is presented in Table 1. These MDLs were determined using a signal/noise ratio of approximately 2:1 with lower and lower amounts of each nitro compound being injected

and detected. As initially suggested in Figure 3, the MDLs *via* FID and ECD are approximately equal within each detector category. However, the PID MDLs are vastly different from one another. This is a direct reflection of the differences in RRFs for these four nitro derivatives on the PID, as discussed further below.

**Table 1: MINIMUM DETECTION LIMITS FOR FOUR TYPICAL NITRO COMPOUNDS (ng)<sup>a</sup> ON THREE TYPICAL GC DETECTORS**

Compound	Detector Type		
	FID	PID	ECD
NITROPENTANE	1.06	0.00 <sup>b</sup>	0.14
NITROCYCLOHEXANE	1.04	0.00 <sup>b</sup>	0.03
O-NITROTOLUENE	0.93	0.40	0.03
2,6-DINITROTOLUENE	1.13	2.80	0.01

a. GC conditions used a 6-ft x 2.0-mm i.d. packed glass column of Ultrabond 20M operated from 50°C to 180°C at 10°C/min with nitrogen carrier gas flow rate of 40 ml/min total.

b. 0.00 indicates that there was no apparent response for these compounds at any level below 1  $\mu$ g injected on-column *via* PID detection.

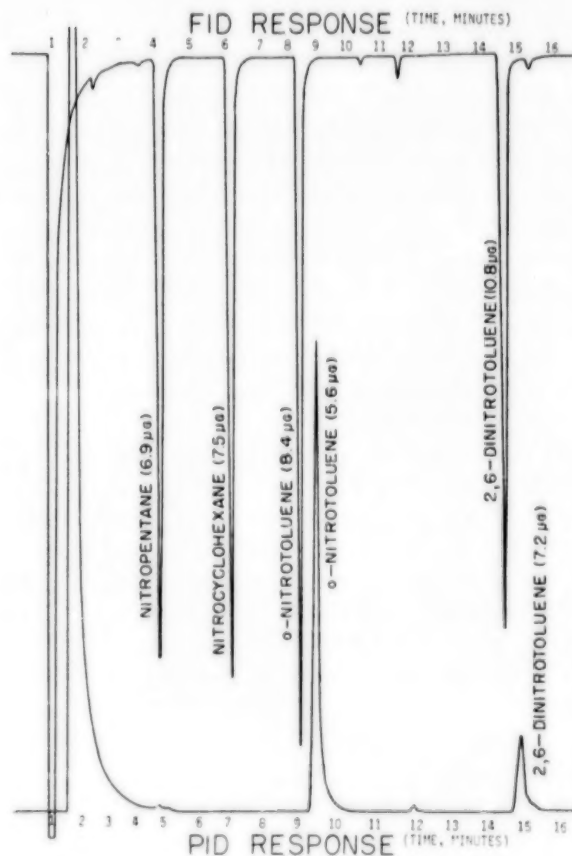


Figure 3. GC-FID/PID chromatograms of four standard nitro organics using a 6-ft x 2.0-mm i.d. packed glass column of Ultrabond 20M, with temperature programming from 50°C (2 mins) to 180°C at 10°C/min, with a final hold at 180°C until elution of fourth analyte. Injector and detector temperatures were 230°C–250°C. Carrier gas flow rate, nitrogen, was about 40 ml/min, with a 70/30 split between FID/PID. Amounts indicated are those reaching each detector.

#### Separations of Nitro Derivatives on Permabond Packing Materials

All of the remaining data for normalized relative response factors on ECD and PID, as well as the ratios of RRFs for ECD/PID, for nitro aromatics, PAHs, and nitro-PAHs, have been determined using either the Permabond Methyl Silicone or Permabond PEG 20M packing materials. Figure 4 is a GC-ECD/PID set of chromatograms for the three mono-nitrotoluene isomers (o-, m-, and p-), together with the specific GC-detector operating conditions and parameters. The amounts indicated are those going to each detector, taking into account the known/determined split ratio of the GC effluent before the detectors. Knowing the absolute split ratio throughout the temperature programmed analysis, the absolute amounts of each compound injected, and the determined peak heights at each recorder/detector attenuation setting, it was possible to calculate relative factors for individual compounds. We have taken o-nitrotoluene as the reference compound, and all other ECD and PID responses are then referenced to o-nitrotoluene as being 1.00 on each detector. Thus, relative response factors, RRFs, are determined directly by measuring peak heights and absolute amounts of each compound reaching that detector. The ratio of peak heights (mm/cm) divided by the number of ng or  $\mu$ g reaching that

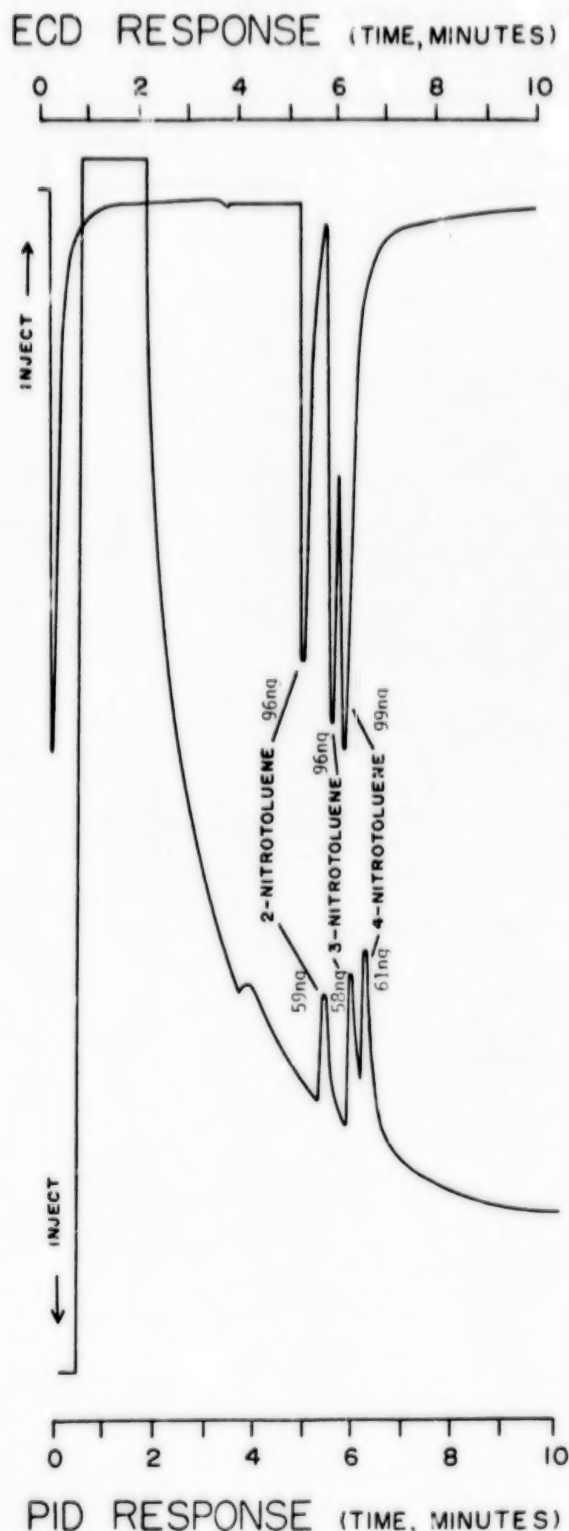


Figure 4. GC-ECD/PID chromatograms of the three mono-nitrotoluene isomers using a 6-ft x 2.0-mm i.d. packed glass column of Permabond Methyl Silicone operated from 50°C to 180°C with temperature programming of 10°C/min. Nitrogen carrier gas flow rate of about 30-40 ml/min with a split ratio between the PID/ECD detectors of about 40/60. Amounts indicated are those reaching each detector.

same detector then provides us with normalized response factors. Normalized relative response factors are simply obtained by using the relative response factor for *o*-nitrotoluene as 1.00 and referencing all other RRFs to that value. This is the origin of our determinations of normalized RRFs. Quite naturally, such calculations are based on detector responses measured or corrected at the same attenuation settings on detector amplifier and recorder.

Table 2 summarizes the RRFs on ECD and PID for the above mono-nitrotoluenes, as well as a variety of other dinitrotoluene isomers and dinitrobenzene isomers, as described further below. For these two detectors, the RRFs within each group of aromatic nitro derivatives are about the same, and therefore the ratio of RRFs for ECD/PID are also about the same for each group. Thus, for similar aromatic nitro isomers, neither the PID nor the ECD provide greatly improved selectivity over the FID. However, Table 2 demonstrates that wherein one compares the ratios of RRFs for ECD/PID between these three classes of aromatic nitro derivatives, this does offer a unique handle for characterizing each separate class. That is, the mono-nitrotoluenes are clearly distinguishable from the dinitrobenzenes, since these do not show any response at these levels on the PID. For the dinitrotoluenes, their ECD/PID ratios of RRFs are again quite different from the other two groups of nitroaromatics in Table 2. Although this approach of using ratios of detector responses, after normalization, has been suggested by others for other classes of organic compounds, its value and analytical utility has rarely been as clearly demonstrated as for the organic nitro compounds, Table 2.

For the GC-ECD/PID analyses of all other groups of nitro aromatics, PAHs, or nitro-PAHs, we have utilized *o*-nitrotoluene as an internal standard always present in the mixtures being analyzed. Figure 5 is a superimposed combination of two separately obtained chromatograms, but both being obtained under identical GC conditions. Because the ECD and PID detector responses to the dinitrotoluene isomers were so very different, it was not possible, with the fixed ratio splitter used, to obtain both ECD and PID chromatograms via a single injection of these compounds. With a variable ratio splitter in place of the fixed ratio one, this problem could have been overcome and both chromatograms could have been obtained via a single injection. However, variable ratio splitters



**Table 2. RELATIVE RESPONSE FACTORS FOR NITRO AROMATICS VIA GC-ECD/PID<sup>a,b</sup>**

Compound	Relative Response Factors (RRFs) <sup>c</sup>		
	PID	ECD	ECD/PID <sup>d</sup>
O-NITROTOLUENE	1.00	1.00	1.00
m-NITROTOLUENE	1.06	1.11	1.05
p-NITROTOLUENE	1.56	1.06	0.68
2,3-DINITROTOLUENE	$2.92 \times 10^{-2}$	5.44	186.3
2,4-DINITROTOLUENE	$9.00 \times 10^{-2}$	4.86	540
2,6-DINITROTOLUENE	$2.46 \times 10^{-2}$	5.47	222.4
3,4-DINITROTOLUENE	$1.78 \times 10^{-2}$	4.94	277.5
O-DINITROBENZENE	----- <sup>e</sup>	4.86	----- <sup>e</sup>
m-DINITROBENZENE	----- <sup>e</sup>	3.31	----- <sup>e</sup>
p-DINITROBENZENE	----- <sup>e</sup>	5.81	----- <sup>e</sup>

- Data was obtained using identical GC conditions for both ECD/PID as indicated in Figure 4. Amounts of each compound reaching each detector was determined knowing amounts injected with determined split ratios on each day's runs.
- GC conditions employed a 6-ft x 2.0-mm i.d. packed glass column of Permabond Methyl Silicone with temperature programming.
- Relative response factors (RRFs) were obtained by measuring peak heights (cm) and dividing by absolute amount reaching that detector (ng), to obtain a response factor as cm/ng for each compound. O-Nitrotoluene was assigned an arbitrary value of 1.00 cm/ng, and all other response factors were calculated relative to o-nitrotoluene to obtain final RRFs.
- ECD/PID ratios were obtained by dividing RRFs via ECD and PID for each compound, but using on both ECD and PID the o-nitrotoluene response as 1.00.
- There was no measurable response below ug amounts for any of the dinitrobenzenes on the PID.

do not provide fixed splitting factors, at a given setting, throughout a temperature programmed GC analysis. The specific GC-detector conditions and amounts reaching each detector are indicated, Figure 5. In Figure 5, there is a single peak for both 2,3- and 2,4-dinitrotoluene derivatives, which were not successfully resolved on this packing material. However, relative response factors were obtained by separate injections of each of these two isomers, together with the internal standard, O-nitrotoluene. An improved resolution of all for dinitrotoluene isomers involved here was eventually obtained, as indicated below. The individual RRFs and ratios of ECD/PID RRFs for these four dinitrotoluenes are indicated in Table 2, and these have been compared and discussed, as above.

The minimum detection limits for the mono-nitrotoluenes, dinitrotoluenes, and dinitrobenzenes, on both ECD and PID, are indicated in Table 3, using GC conditions described above, Figures 4 and 5. In each instance, the MDLs *via* ECD are orders of magnitude lower than *via* PID. It is generally realized that for organic nitro compounds, detection limits will always be lower on the ECD than the PID. However, compound identification and detector selectivity will generally be better *via* the PID rather than the ECD. In deciding which detector is to be most useful for organic nitro compound analysis, one must first decide whether it is detectability or selectivity that is of greater concern.

**Table 3. MINIMUM DETECTION LIMITS FOR ISOMERIC NITRO DERIVATIVES VIA GC-ECD/PID<sup>a</sup>**

Compound	Detector Type	
	ECD (ng)	PID
o-NITROTOLUENE	0.022	5.95 ng
m-NITROTOLUENE	0.020	5.61 ng
p-NITROTOLUENE	0.021	3.81 ng
2,3-DINITROTOLUENE	0.003	0.05 ug
2,4-DINITROTOLUENE	0.003	0.162 ug
2,6-DINITROTOLUENE	0.003	0.059 ug
3,4-DINITROTOLUENE	0.003	0.082 ug
o-DINITROBENZENE	0.045	----- <sup>b</sup>
m-DINITROBENZENE	0.066	----- <sup>b</sup>
p-DINITROBENZENE	0.046	----- <sup>b</sup>

- GC conditions used a 6-ft x 2-mm i.d. glass packed column of Permabond methyl silicone operated from 50-180°C at 10°C/min with carrier gas flow rate of 35-40 ml/min. Detection limits were determined by injecting lower and lower absolute amounts of each compound using a final signal/noise ratio of 2/1 at the lowest attenuations possible or feasible.
- Indicates that there was no apparent response for these compounds at any level below 1 ug injected on-column via PID detection.

The Permabond Methyl Silicone packing material has also been utilized for the resolution and detection *via* ECD/PID of several typical polycyclic aromatic hydrocarbons (PAHs) and their nitro-derivatives (nitro-PAHs). Figure 6 is a GC-PID chromatogram of five PAHs together with o-nitrotoluene as the internal standard, with the amounts indicated going to the PID. Specific

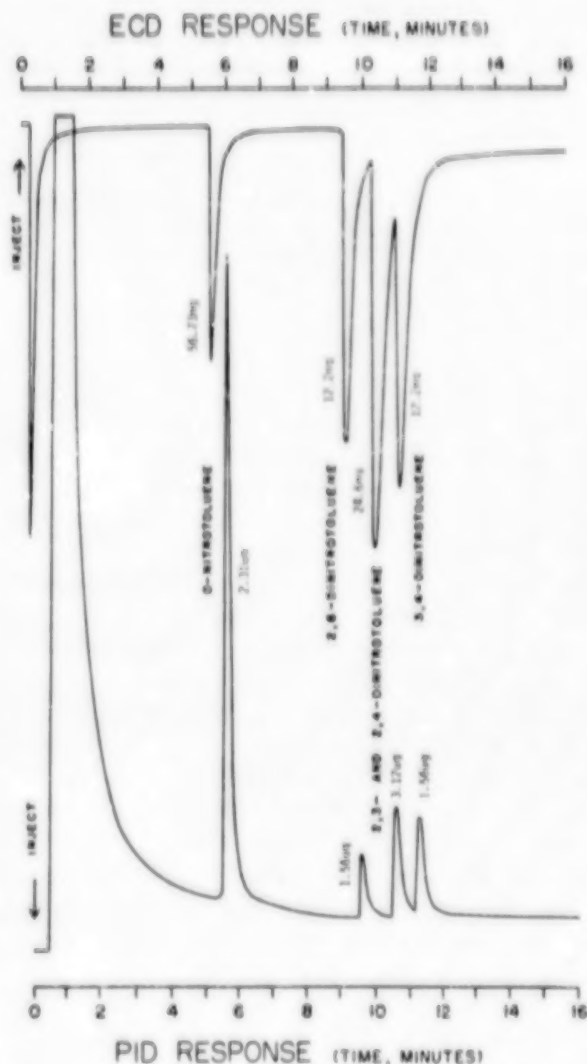


Figure 5. GC-ECD and GC-PID chromatogram for mixture of *o*-nitrotoluene and three dinitrotoluene isomers. The individual GC chromatograms were superimposed on top of one another for ease of comparison between the two detectors. GC conditions in each case used a packed glass column, 6-ft x 2.0-mm i.d., of Permabond Methyl Silicone, operated from 50°C to 180°C at 10°C/min, with a nitrogen carrier gas flow rate of 40 ml/min. Amounts indicated are those reaching each detector. GC eluent split ratio between PID/ECD was 40/60.

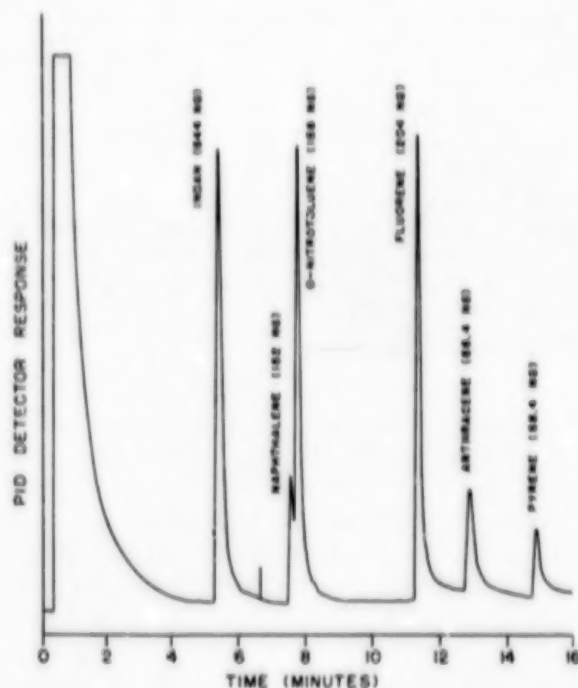


Figure 6. GC-PID chromatogram of a mixture of polycyclic aromatic hydrocarbons with *o*-nitrotoluene as internal standard. GC conditions used a 6-ft x 2.0-mm i.d., packed glass column of Permabond Methyl Silicone operated from 40°C to 225°C at 15°C/min with temperature programming. Nitrogen carrier gas flow rate of 15 ml/min to PID.

GC conditions for this determination are indicated in the Figure. Although naphthalene is not baseline resolved from *o*-nitrotoluene, the relative peak heights can be accurately determined, together with relative response factors for all of the PAHs involved. As expected, PAHs respond considerably better on the PID than on the ECD, and these relative response factors have been summarized in Table 4 for both the PAHs and nitro-PAHs of interest here.

Table 4. RELATIVE RESPONSE FACTORS (RRFs) AND ECD/PID RATIOS FOR PAHs AND THEIR NITRO-PAH ANALOGS

Compounds	ECD	PID	ECD/PID <sup>a</sup>
<i>o</i> -NITROTOLUENE	1.00	1.00	1.00
INDAN	$7.18 \times 10^{-5}$	$5.4 \times 10^{-1}$	$1.34 \times 10^{-4}$
5-NITROINDAN	2.32	1.18	1.97
NAPHTHALENE	$8.01 \times 10^{-6}$	$2.86 \times 10^{-1}$	$2.80 \times 10^{-5}$
2-NITRONAPHTHALENE	4.73	1.25	3.78
FLUORENE	-----	$7.62 \times 10^{-1}$	-----
2-NITROFLUORENE	3.48	$7.5 \times 10^{-1}$	4.64
ANTHRACENE	$6.73 \times 10^{-3}$	$5.20 \times 10^{-1}$	$8.83 \times 10^{-3}$
9-NITROANTHRACENE	2.50	1.38	1.81
PYRENE	$1.53 \times 10^{-2}$	$3.88 \times 10^{-1}$	$3.94 \times 10^{-2}$

**Table 4. RELATIVE RESPONSE FACTORS (RRFs) AND ECD/PID RATIOS FOR PAHs AND THEIR NITRO-PAH ANALOGS—Cont.**

Compounds	ECD	PID	ECD/PID <sup>b</sup>
3-NITROPYRENE	2.18	$3.70 \times 10^{-1}$	5.89
o-NITROTOLUENE	1.00	1.00	1.00

- GC conditions used a 6-ft x 2.0-mm i.d. packed glass column of Permabond Methyl Silicone operated with temperature programming from 40°C to 225°C at 15°C/min with nitrogen carrier gas flow rate of 15 ml/min.
- All calculations were done using peak heights and not peak areas. ECD and PID responses were first normalized to that of o-nitrotoluene at 1.00 (cm/ng) knowing amounts of each compound injected, detector attenuations, and peak heights obtained (cm). Analyzed as mixtures of PAHs or nitro-PAHs with o-nitrotoluene present as internal standard.
- It was not possible to obtain any measurable ECD response for fluorene at ug levels or above reaching the ECD.

Figure 7 is a combination of two superimposed GC-ECD and GC-PID chromatograms for a mixture of five different nitro-PAHs with o-nitrotoluene as the internal standard. These two chromatograms were obtained separately, using identical GC conditions, but with different levels of the nitro-PAHs injected as a function of the detector in use. The final two chromatograms have then been purposely superimposed in order to be able to make direct detector comparisons more apparent. GC conditions are indicated in Figure 7 and above (Experimental). Although 2-nitrofluorene and 9-nitroanthracene have not been baseline resolved in Figure 7, separate injections of each of these alone enabled the determination of relative response factors vs o-nitrotoluene for each detector.

A summary of the PAH and nitro-PAH relative response factors for ECD and PID is indicated in Table 4, wherein these have been normalized and related to o-nitrotoluene as the base response of 1.00 on both detectors. This provides the data in the first two columns, and when the ratio of these normalized RRFs are taken, the final column headed ECD/PID can be obtained, Table 4. It is immediately apparent that the PAHs respond orders of magnitude better on the PID than on the ECD, and that the nitro-PAHs have responses on the ECD that are, in general, an order of magnitude or so better (more intense) than on the PID.

That is, these two classes of compounds respond in opposite directions, with regard to sensitivity, for these two particular detectors. When the ratios of RRFs for ECD/PID, column three in Table 4, are calculated, the overall differences between the PAHs and their nitro-PAH derivatives can be several orders of magnitude. Table 5 makes this last comparison directly, wherein for each pair of PAH and nitro-PAH, their respective PID/PID and ECD/ECD ratios are presented in columns 1 and 2. The final column in Table 5, *viz.*, the respective ECD/PID-ECD/PID ratios from Table 4 for each pair of PAH and nitro-PAH are indicated. That is, the ECD/PID ratio from Table 4 for a particular PAH is divided by the analogous ECD/PID ratio for its direct nitro-PAH analog (indan/5-nitroindan). It is just this final column of Table 5 that is of most interest, because it for the first time indicates that ECD/PID ratios can be 3 to 6 orders of magnitude different between any given PAH and its corresponding nitro-PAH. This suggests an unusually high degree of selectivity for any particular PAH and its nitro derivative *via* GC-ECD/PID relative response factors and their derived ratios, Table 5. Since many environmental samples have already been shown to contain PAHs together with nitro-PAHs, this approach should provide a new method of confirming the class of compounds that an unknown GC peak may belong to.



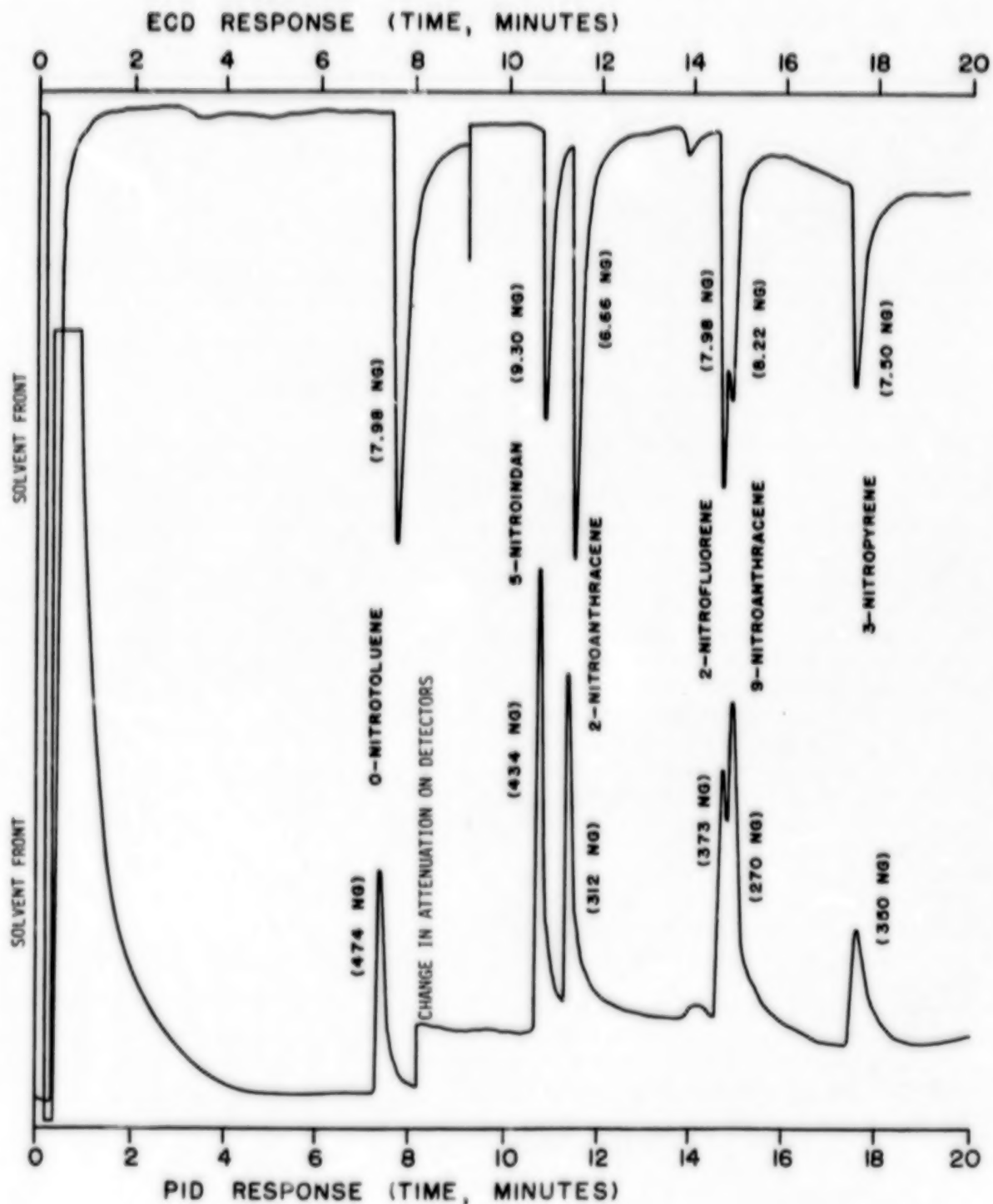


Figure 7. GC-ECD/PID combined (superimposed) chromatograms for a mixture of PAHs and nitro-PAHs with o-nitrotoluene as internal standard. GC conditions used a 6-ft x 2.0-mm i.d., packed glass column of Permabond Methyl Silicone operated from 40°C to 225°C at 15°C/min with temperature programming. Nitrogen carrier gas flow rate of 40 ml/min split ECD/PID.

Table 5. RELATIVE RESPONSE FACTOR RATIOS ON ECD/PID FOR PAHs AND NITRO-PAHs

Compound Pair	PID/PID	ECD/ECD	ECD/PID-ECD/PID <sup>b</sup>
INDAN/5-NITROINDAN	$4.6 \times 10^{-1}$	$3.1 \times 10^{-5}$	$6.80 \times 10^{-5}$
FLUORENE/2-NITROFLUORENE	1.01	-----	-----
NAPHTHALENE/2-NITRO-NAPHTHALENE	$2.3 \times 10^{-1}$	$1.70 \times 10^{-6}$	$7.41 \times 10^{-6}$
ANTHRACENE/9-NITRO-ANTHRACENE	$3.8 \times 10^{-1}$	$2.70 \times 10^{-3}$	$4.88 \times 10^{-3}$
PYRENE/3-NITROPYRENE	1.00	$7.0 \times 10^{-3}$	$6.69 \times 10^{-3}$

- a. ECD/PID relative response factor ratios were obtained on a 6-ft x 2.0-mm i.d. packed glass column of Permabond Methyl Silicone operated from 40°C to 225°C at 15°C/min with temperature programming and a nitrogen carrier gas flow rate of 15 ml/min. Analyzed as mixtures of PAHs or nitro-PAHs with o-nitrotoluene present as internal standard.
- b. All calculations were done using peak heights and not peak areas. Relative response factor normalizations were done using o-nitrotoluene as 1.00 on both ECD and PID.
- c. It was not possible to obtain any measurable ECD response for fluorene at ug levels or above reaching the ECD.

The above analyses and detector response factors for these nitro aromatics, PAHs, and nitro-PAHs have been repeated on another Permabond PEG 20M type packing material, with GC separation conditions as indicated in Figure 8. This is a reconstructed GC-ECD/PID set of chromatograms, wherein the GC-ECD and GC-PID chromatograms were obtained separately *via* two injections of the same mixture of nitro derivatives, but utilizing different levels for each injection. The final two chromatograms have been superimposed to yield Figure 8 for simplicity's sake. Whereas it was not previously possible to baseline resolve 2,3- and 2,4-dinitrotoluene isomers, Figure 5, with the Permabond PEG 20M packing material, this separation is readily achieved. Determinations of RRFs, normalized RRFs, and ECD/PID ratios of RRFs, as above, have now been made with the Permabond PEG 20M separations, and these results are very similar to those already presented, Table 2.

Figure 9 is the GC-ECD chromatogram of a mixture of the three dinitrobenzene isomers together with o-nitrotoluene, again using a Permabond PEG 20M packing material with the specific operating conditions indicated. These nitroaromatics show no response on the PID at or below ug levels reaching the PID.

The final chromatogram described here, Figure 10, is the GC-PID chromatogram of five typical PAHs together with o-nitrotoluene as internal standard. These have been separated on a Permabond PEG 20M column, with the specific conditions as indicated in this Figure. The separation of naphthalene from the o-nitrotoluene is somewhat better on the Permabond PEG 20M than it was on the Permabond Methyl Silicone, as above, Figure 6.

The almost unequivocal identification of a nitroaromatic or nitro-PAH can be realized using the above ECD/PID ratios of normalized RRFs, together with single derivatization reaction de-

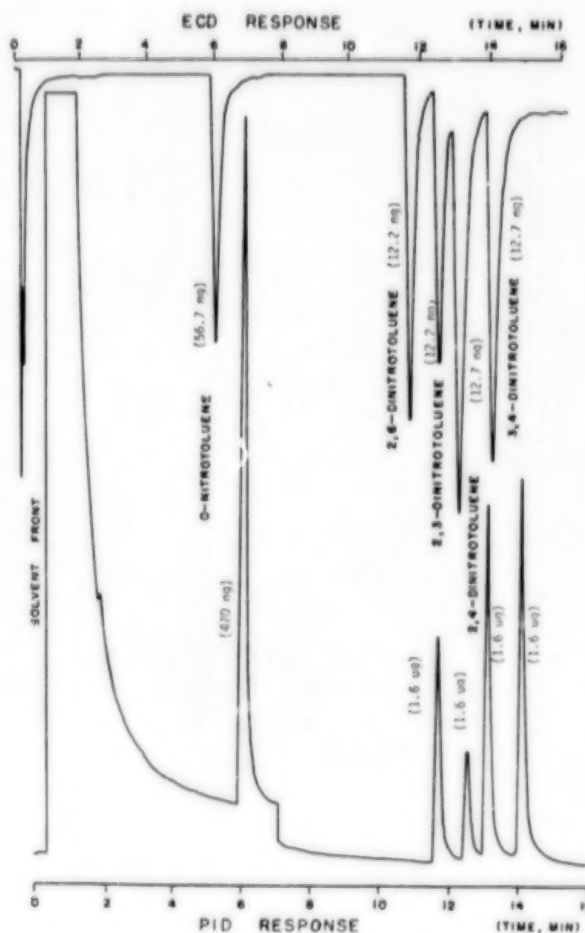


Figure 8. GC-ECD/PID superimposed chromatograms of four isomeric dinitrotoluenes plus o-nitrotoluene analyzed on a 6-ft x 2.0-mm i.d. packed glass column of Permabond PEG 20M at 10°C/min from 50°C to 180°C with nitrogen carrier gas flow rate of 35-40 ml/min.

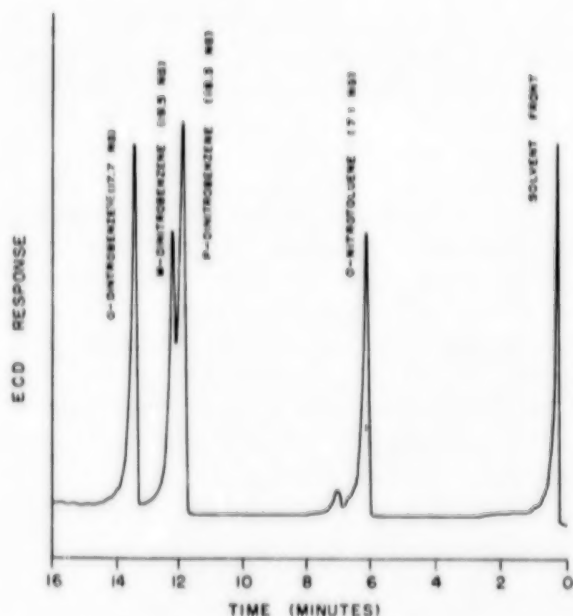


Figure 9. GC-ECD chromatogram of the three dinitrobenzene isomers with o-nitrotoluene as internal standard, obtained on a 6-ft x 2.0-mm i.d. packed glass column of Permabond PEG 20M operated from 50°C to 180°C at 10°C/min with a carrier gas flow rate of 35-40 ml/min total. Amounts indicated are those reaching the detector.

signed to convert the nitro group to an amino substituent. A large number of useful and easy-to-apply chemical reductions have been described in the literature that will effect the conversion of a nitroaromatic into an aminoaromatic derivative. We have now applied this type of single-step derivatization to a large number of nitroaromatics, as described above, and have then compared the RRFs for the starting nitro compound with the known/expected amine product.

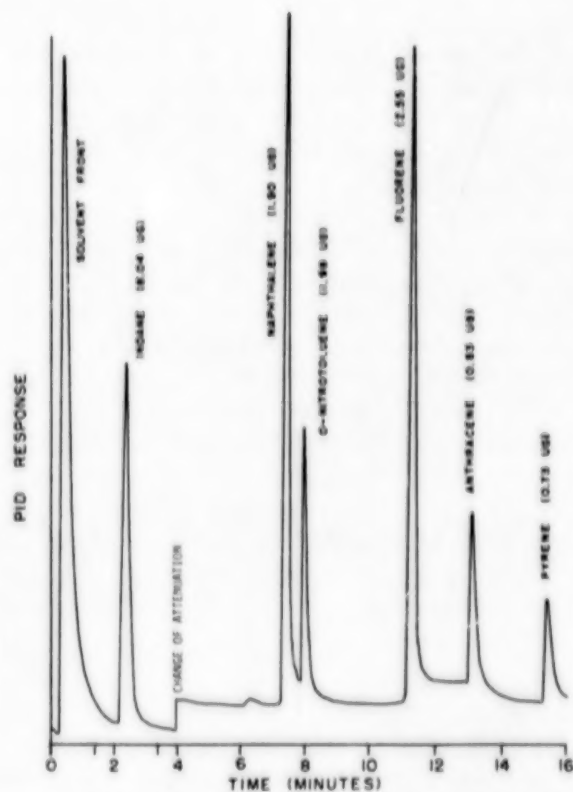


Figure 10. GC-PID chromatogram of five typical PAHs plus o-nitrotoluene on a 6-ft x 2.0-mm i.d. packed glass column of Permabond PEG 20M operated at 15°C/min from 40°C to 225°C with a total carrier gas flow rate of 35-40 ml/min. Amounts indicated are those reaching the detector.

At the same time, it has been possible to obtain ratios of ECD/PID RRFs, as already described for the nitro-PAHs and PAHs above, and these results are indicated in Table 6. The farthest column on the right of Table 6 indicates the ratios of ECD/PID RRFs for each amine/nitro compound

Table 6. NORMALIZED RELATIVE RESPONSE FACTORS VIA GC-ECD/PID FOR VARIOUS AROMATIC AMINE/NITRO TYPE COMPOUNDS<sup>a</sup>

Compound Studied <sup>b</sup>	RRF-ECD	RRF-PID	RRF-ECD/PID	Amine/Nitro Pair Ratio <sup>c</sup>
p-TOLUIDINE	$8.64 \times 10^{-4}$	0.585	$1.45 \times 10^{-3}$	$4.62 \times 10^{-4}$
p-NITROTOLUENE	1.46	0.465	3.14	
2,6-DIAMINOTOLUENE	$1.54 \times 10^{-3}$	1.81	$8.53 \times 10^{-4}$	$3.84 \times 10^{-6}$
2,6-DINITROTOLUENE	5.47	$2.46 \times 10^{-2}$	222.4	
2,4-DIAMINOTOLUENE	$3.61 \times 10^{-3}$	1.77	$3.52 \times 10^{-3}$	$6.52 \times 10^{-6}$
2,4-DINITROTOLUENE	4.86	$9.00 \times 10^{-2}$	540.0	
2-AMINOFLUORENE	$9.48 \times 10^{-3}$	1.79	$5.30 \times 10^{-3}$	$1.14 \times 10^{-3}$
2-NITROFLUORENE	3.48	0.750	4.64	
5-AMINOINDAN	$1.66 \times 10^{-3}$	3.26	$5.09 \times 10^{-4}$	$2.58 \times 10^{-4}$
5-NITROINDAN	2.32	1.18	1.97	

- Relative response factors were calculated using an internal standard, o-nitrotoluene as the base compound response on both ECD/PID, normalizing all such responses on a per ng or per ug basis, and then making these relative to the internal standard as 1.00 on each detector.
- All compounds studied were obtained commercially, of the highest purity available.
- GC conditions used a Permabond Methyl Silicone column, 6-ft x 2.0-mm i.d., glass packed, with temperature programming in all cases.

pair. These are seen to be orders of magnitude different, ranging from three to six orders in such overall ratio differences. Thus, the use of this type of derivatization for nitroaromatics, perhaps for nitro aliphatics, can provide yet further characterization and speciation for unknown nitro compound present in complex sample matrices.

With regard to the utilization of the above analytical approaches for the identification and characterization of various explosives, we have studied four such compounds in dual ECD/PID detection in GC. Table 7 summarizes the RRFs *via* ECD and PID for these four compounds, again using o-nitrotoluene as the internal standard of reference.

At the same time, we have determined the normalized ECD/PID ratios of RRFs, farthest column on the right in Table 7, which again provides quantitative data to identify an individual explosive that may be present in a complex sample matrix. In some cases, the explosive of interest, such as TNT or RDX, does not respond at all on the PID, but does, as expected, on the ECD. In other cases, tetryl and NG, there are satisfactory detector responses on both ECD/PID, and one can then obtain a quantitative ratio of these RRFs, as indicated. Thus, at least these four explosives provide widely different ECD/PID ratios of RRFs, data which could be used to differentiate one explosive from another/others.

**Table 7. RELATIVE RESPONSE FACTORS AND ECD/PID RATIOS FOR EXPLOSIVES<sup>a</sup>**

Compound Name <sup>c</sup>	RRF-ECD	RRF-PID	RRFs-ECD/PID <sup>d</sup>
o-NITROTOLUENE	1.00	1.00	1.00
TNT	4.36	---- <sup>b</sup>	----
RDX	1.60	----	----
TETRYL	3.00	$6.13 \times 10^{-3}$	48.94
NG	0.109	$6.71 \times 10^{-3}$	16.24

a. GC conditions used a 6-ft x 2.0-mm i.d. glass packed column of PermaBond Methyl Silicone operated from 50°C to 260°C at a temperature program of 15°C/min with a nitrogen carrier gas flow rate of 22ml/min.

b. These explosives did not respond on the PID at ug levels or below.

c. Compound names: TNT = 2,4,6-trinitrotoluene; RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane; TETRYL = 2,4,6,N-tetranitro-N-methylaniline; NG = nitroglycerin.

d. Calculations of normalized RRFs for these explosives were performed as described above for the other nitro derivatives, nitro-PAHs, etc.

Clearly, the data presented above is only useful wherein the amounts of each nitroaromatic, PAH, and nitro-PAH reaching the detectors are within the linear portion of the calibration plot for such compounds on each detector. If amounts injected exceed such linear regions of the calibration plots, then the ECD/PID ratios so obtained would not be valid or reproducibly useful and/or applicable. Thus, for the analyst to use this approach he must first demonstrate that he is indeed working within the linear portion of his calibration plots for each compound of interest with each detector used. This has been demonstrated for all of the above compounds/data, wherein individual calibration plots have been obtained for at least one member of each class or group of nitro derivatives. The amounts of each compound reaching the two detectors in each and every case/study have now been shown to fall within the linear portion of the respective and applicable calibration plots. This is important to remember whenever ratios of detector responses are to be used as a method of analyte identification and/or confirmation.

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## DETERMINATION OF NITRO EXPLOSIVES BY GAS CHROMATOGRAPHY UTILIZING AN ON-COLUMN CAPILLARY INJECTOR

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**ABSTRACT.** Nitroglycerin and other nitrated esters are important compounds because of their use as explosives and as drugs in the treatment of cardiac disorders. The compounds have been determined by gas chromatography using conventional packed columns but the analysis can be quite difficult. Temperatures must be carefully controlled and the column must be prepared and conditioned very carefully so that active sites on which the nitrated esters can decompose are eliminated. Capillary columns made of fused silica (pure synthetic  $\text{SiO}_2$  without metal contaminants) have been found to be of value when analyzing reactive compounds. When combined with a capillary on-column injector, many compounds that could not be analyzed by gas chromatography or could only be determined with great difficulty can now be measured. In this study, an electron capture detector was used and nitroglycerin was determined down to sub-picogram levels. The sample was injected directly into the fused silica column under non-vaporizing conditions. There was no sign of tailing or decomposition. Linearity of response was examined over a concentration range of  $10^{-3}$  and the correlation coefficient to a straight line was 0.997. In the discussion, the on-column injection technique will be described and contrasted with the older capillary injection techniques (split and splitless). Problems that one might encounter will be mentioned and results with other explosives such as nitramine and pentaerythritol tetranitrate will be given.

Since the late 1970's, improvements have occurred in the techniques of gas chromatography so that compounds of higher molecular weight and greater reactivity may be determined. The widespread use of fused silica capillary columns came first, followed by changes in the capillary inlet systems. It is now possible to introduce a sample directly into a fused silica column at temperatures well below the boiling point of all of the components. Thus gas chromatography has become a very practical technique for separating explosives.

In this paper, the advantages of capillary gas chromatography with on-column injection will be described. The features of the Varian on-column injector will also be mentioned. In addition, the chromatographic conditions and results obtained in the separation of some nitro explosives will also be covered. The method is suitable for trace analysis—the minimum detectable quantity of nitroglycerine is less than one picogram injected onto the column.

### Advantages of Capillary Columns and On-Column Injection

In general, in almost any gas chromatographic analysis, capillary columns have many advantages over packed columns. Capillary columns offer far better resolution, resulting in relatively tall narrow peaks. The result is better separation of compounds of interest from interfering peaks, lower detection limits, and less errors in quantitation. Most capillary columns presently used are made of pure silicon dioxide without the metal contaminants found in glass columns. The purity of the material of which the column is constructed results in less tailing of polar compounds and less breakdown of reactive compounds.

The technique of injecting the sample directly into a fused silica column under non-vaporizing conditions offers advantages over the traditional split-splitless inlet. These inlets are basically flash injectors—the sample is normally introduced into

a hot glass<sup>1</sup> liner where it evaporates quickly. Under these conditions, decomposition of labile compounds may occur as well as absorption of polar compounds on the hot glass liner or in the heated needle. For samples of wide boiling point range, discrimination also occurs in a split/splitless injector. The lowest boilers tend to evaporate prematurely and the highest boilers tend to remain in the needle so that the medium boilers are over-represented in the chromatogram. Cold on-column injection has been shown by Schomberg *et al.* (1981) to result in less mass discrimination than any other capillary injector technique.

The Varian 1095 on-column injector (Figure 1) has several features that are worth mentioning. One of these features is an inlet that is sealed at all times. This prevents loss of very volatile compounds and makes flow controlled pneumatics possible. Thus, during temperature programming, the carrier gas flow remains constant and late eluting compounds come out somewhat sooner and with less peak broadening than would be possible in a pressure controlled system. The injector is also encased in a unit that allows cooling with liquid CO<sub>2</sub> or N<sub>2</sub> down to 0° Celsius and temperature programming at a rate of 20° to 180° per minute up to 350°. This cooling and heating is entirely separate from the column oven. The sample is introduced with a 5 µl syringe that contains a replaceable fused silica needle. The upper two-thirds of the needle is encased in a stainless steel sheath. The system is closed to the atmosphere when the sheath enters the Teflon seal in the top portion of the injector. Table 1 shows results obtained with this injector for analysis of straight chain alkanes.

#### Chromatographic Equipment and Conditions for Determination of Nitro Explosives

The analyses were performed with a Varian 6000 gas chromatograph equipped with a Model 1095 on-column injector and electron capture detector. A Varian 401 chromatography data system was used for quantitation.

The column was 0.32 mm x 12 meter fused silica coated with SE 30. A column was deliberately chosen with a film thickness of 0.5 micron<sup>2</sup> to minimize the possibility that exposed fused silica would contact the explosives and cause degradation. It was necessary to use a new column that

<sup>1</sup> Some metal may also be present.

<sup>2</sup> Several film thicknesses are commercially available—the most common is 0.25 micron.

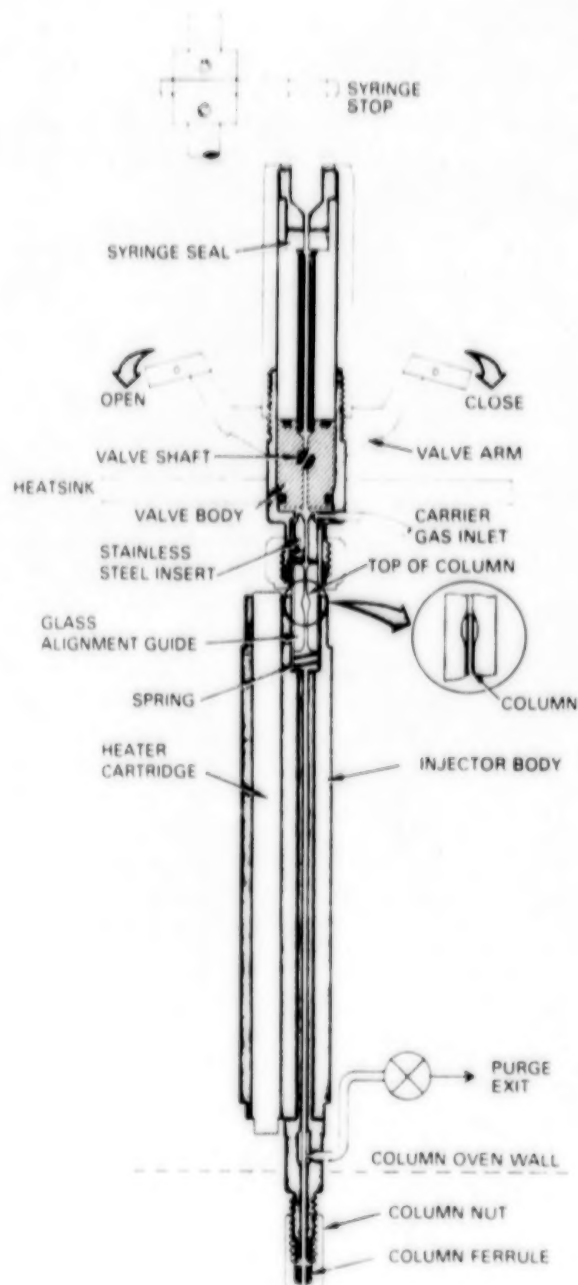


Figure 1. Cross sectional diagram of the Varian on-column capillary injector. The fused silica column is inserted through the bottom and terminates in the wide portion of the glass alignment guide. The fused silica needle penetrates about 3 cm into the column.

had never been heated above 250°. If a good column was used at the beginning and never overheated, column life appeared reasonable—no degradation was evident after two months of use.

An electron capture detector is necessary for trace analysis (< 1 nanogram injected). For larger quantities (1-200 nanograms), a flame ionization detector may be used. A nitrogen-specific detector

**TABLE 1. ACCURACY AND PRECISION FOR A WIDE BOILING RANGE MIXTURE OF NORMAL HYDROCARBONS WITH TEMPERATURE PROGRAMMED CAPILLARY ON-COLUMN INJECTION.**

Column: 15 M x 0.32 mm DB-5, 6 ml/min H<sub>2</sub> carrier gas, flow controlled.

Averages of 5 consecutive runs.

Oven: 70°C initial, 10°C/min to 300°C.

Injector: 70°C initial, 100°C/min to 300°C.

Sample: Nominally 40 ng/μl each n-alkanes in isooctane. 0.5 μl injected.

	Factor	% R.S.D.	Retention Time, Minutes	R.S.D. Seconds N = 5	% R.S.D.
n-C <sub>12</sub>	0.996	1.15	3.249	0.20	0.103
n-C <sub>14</sub>	0.999	0.679	5.592	0.16	0.047
n-C <sub>16</sub>	0.979	0.627	7.846	0.15	0.031
n-C <sub>18</sub>	0.997	0.211	9.912	0.15	0.032
n-C <sub>22</sub>	1.00	—	13.529	0.16	0.020
n-C <sub>26</sub>	0.994	0.314	16.612	0.24	0.024
n-C <sub>30</sub>	1.020	0.187	19.298	0.25	0.022
n-C <sub>36</sub>	1.020	0.714	22.751	0.31	0.023
n-C <sub>40</sub>	0.999	0.512	24.896	0.42	0.028
n-C <sub>44</sub>	1.010	0.950	28.500	0.43	0.025

responded only to compounds in which there was a carbon to nitrogen bond and therefore was not suitable for nitroglycerine or pentaerythritol tetranitrate (Figure 2).

GC conditions:

Column oven: 40°C initial temperature, programmed at 20°C/minute to 160°C, hold five

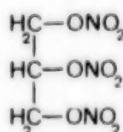
minutes.

On-column injector: 40° initial temperature, programmed at 60°C/minute to 160°C, hold nine minutes.

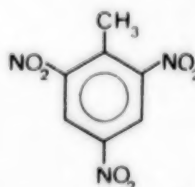
Electron capture detector: 180°, range 10.

Carrier gas: Helium, 4.5 ml/minute.

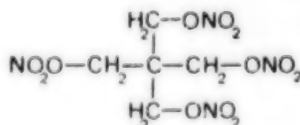
Detector makeup gas: Nitrogen, 30 ml/minute.



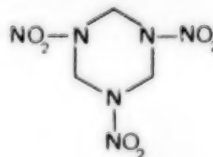
**NITROGLYCERINE**



**TRINITROTOLUENE  
TNT**

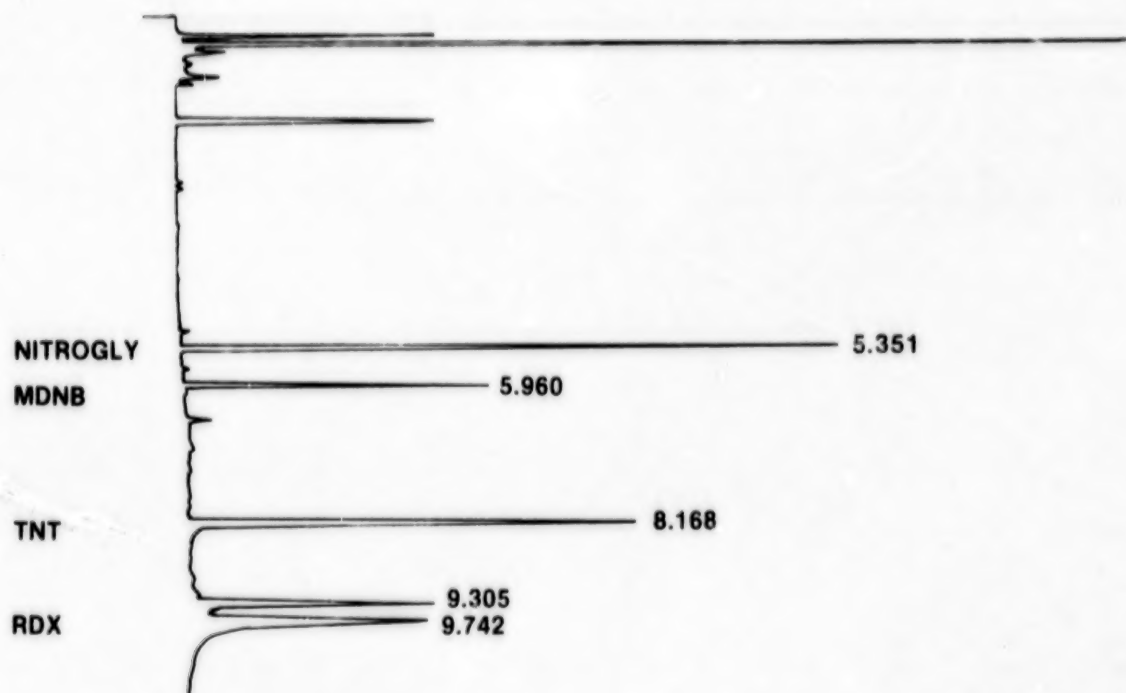


**PENTAERYTHRITOL TETRANITRATE  
PETN**



**CYCLOTRIMETHYLENETRINITRAMINE  
RDX**

Figure 2. Structure of the explosive nitro compounds separated in this study.



# **TITLE: EXPLOSIVE STANDARDS**

**CHANNEL NO: 2**

**SAMPLE: STDS**

**METHOD: EXPLOSIVES**

PEAK NO	PEAK NAME	RESULT NG/ML	TIME (MIN)	TIME OFFSET	AREA COUNTS	SEP CODE	W1/2 (SEC)
1	NITROGLY	101.6400	5.351	-0.009	67126	VV ?	0.80
2	MDNB	INT STD	5.960R	-0.010	31572	BV	1.45
5	TNT	200.8060	8.168	-0.012	98367	BB ?	1.80
7	PETN	412.1790	9.478	-0.012	77665	VV ?	3.70
8	RDX	407.7500	9.742	-0.018	127964	VB ?	7.05
<b>TOTALS:</b>		<b>1122.380</b>		<b>-0.061</b>	<b>402694</b>		

Figure 3. Chromatogram and report of the explosive standards separated in this study. Chromatographic conditions are described in the text and in Table II.

## **Results and Discussion**

Figure 3 shows the chromatogram obtained with the explosives mixture and the linearity curves are depicted in Figure 4. Table 2 summarizes the statistical parameters and minimum detectable quantity for each explosive.

In conclusion, nitro explosives at the picogram

level can be measured with reasonable precision and accuracy using an on-column capillary injector, fused silica column, and electron capture detection. This system would be suitable for quantitating these compounds at very low levels such as in hand swabs. For larger quantities, the sample must be diluted or flame ionization detection might be employed.

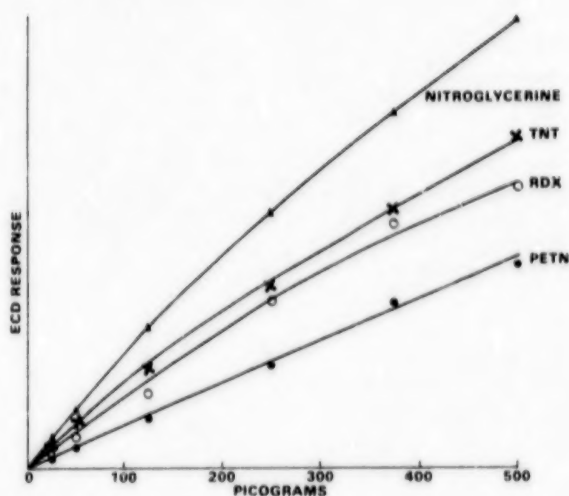


Figure 4. Linearity curves for several explosives. Each point is the average of three determinations. Precision data and correlation coefficient to a straight line are in Table II.

**TABLE 2. LINEARITY, PRECISION AND MINIMAL DETECTABLE QUANTITY DATA FOR NITRO EXPLOSIVES WITH TEMPERATURE PROGRAMMED CAPILLARY ON-COLUMN INJECTION AND ELECTRON CAPTURE DETECTION.**

Column: 12 M x 0.32 mm fused silica coated with 0.5 micron SE 30.

Carrier gas: Helium at 4.5 ml/minute.

Oven: 40°C initial, 20°C/min to 160°C, hold 5 minutes.

Injector: 40°C initial, 60°C/min to 160°C, hold 9 minutes.

Detector: Electron capture at 180°C, range 10, 30 ml/min N<sub>2</sub> makeup gas.

Sample: Dissolved in hexane at various levels, 1.4 microliters injected.

Compound	Correlation coefficient to a straight line 25-500 picograms	% RSD of response factor (relative to m-dinitrobenzene) n = 3	Minimum detectable quantity 4 x noise level (noise was .019 millivolts)
Nitroglycerine	.9982	1.47% (100 pg)	.035 picogram
Trinitrotoluene (TNT)	.9992	0.45% (200 pg)	.11 picogram
Pentaerythritol tetranitrate (PETN)	.9988	3.53% (400 pg)	.38 picogram
Cyclotrimethylene trinitramine (RDX)	.9952	2.85% (400 pg)	.39 picogram

## REFERENCE

Schomburg, G., Husmann, H., and Rittmann, R. (1981). "Direct" (on-column) sampling into glass capillary columns—comparative investigations on split, splitless and on-column sampling. *J. Chrom.* 204: 85-96.

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## DIFFERENTIAL THERMAL ANALYSIS OF PYROTECHNIC COMPOSITIONS

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**ABSTRACT.** Differential thermal analysis (DTA) has proven to be a valuable tool for the identification and qualitative analysis of pyrotechnic and explosive mixtures as well as for the investigation of the chemical mechanism of pyrotechnic reactions. In DTA, processes that absorb heat from the surroundings, such as melting, boiling, and crystalline phase transitions, produce downward peaks, termed endotherms, in a plot of  $\Delta T$  versus  $T$  (temperature difference between sample and thermally-inert reference material). Processes that release heat, such as exothermic reactions, produce upward peaks (exotherms) in the plot. The resulting diagram, upon heating from room temperature to 500, 800, 1200° or higher, is termed a *thermogram*. The pattern for a particular pure material yields a thermal "fingerprint" that can be used for qualitative purposes and for purity determinations. The thermogram also yields information regarding the thermal stability of new materials and mixtures. The thermogram of a pyrotechnic or explosive mixture is a combination of the thermograms of the individual components, up to the ignition temperature of the material. At that point, a strong exothermic peak is observed corresponding to the occurrence of a self-propagating reaction. Typical thermograms of pyrotechnic and explosive materials will be presented, and some of the chemical implications regarding ignition behavior will be discussed.

Differential thermal analysis (DTA) provides a rapid method for obtaining a thermal "fingerprint" of an unknown material. The data obtained from such a study can be used for qualitative identification and for determining the possible explosive nature of an unknown solid material. Thermal analysis techniques can be particularly helpful when working with nonvolatile species, where other instrumental techniques such as gas chromatography/mass spectrometry (GCMS) are not applicable.

In a thermal analysis study, one monitors the difference in temperature,  $\Delta T$ , between the sample and a thermally-inert reference material as the sample and reference are identically heated from room temperature to a predetermined limit, typically 500°C. Thermocouples placed in the sample and reference compartments measure any temperature difference that occurs during the heating process. A temperature difference will be observed if an exothermic or endothermic process occurs in the sample. Melting, boiling, and solid-solid

phase transitions are processes that will momentarily cause the sample to be lower in temperature than the reference material, and a downward deflection—known as an **ENDOTHERM**—is produced in a plot of  $\Delta T$  versus  $T$  (of the heating block). This plot is called a **THERMOGRAM**. Similarly, if an exothermic chemical reaction occurs in the sample, an upward deflection—called an **EXOTHERM**—will be produced.

The pattern of exotherms and endotherms, versus temperature, is characteristic of a particular sample and should be reproducible for a given material under a given set of experimental conditions. This fact makes DTA a valuable tool for the high-energy chemist, with many possible applications including the following:

1. Qualitative identification of unknown materials
2. Rapid indication of purity, by an examination of the position and shape of the melting point endotherm
3. Determination of reaction temperatures, in-

cluding the ignition temperatures of explosives and pyrotechnic materials.

**Note:** Ignition temperatures are quite sensitive to the experimental conditions employed—heating rate and sample size should be specified.

Thermal analysis can therefore provide an abundance of information concerning the identity and reactivity of an unknown material, requiring a sample size of less than 10 mg, no pretreatment of the sample, and an analysis time of approximately 10 minutes. Because of the small sample size, DTA is one of the safest techniques for laboratory personnel to use with unknown materials.

The typical thermal pattern for unstable molecular solids is an endotherm for the melting point, followed by an exothermic decomposition at a temperature usually well below 500°C. Most common "high explosive" species—such as TNT, PETN, and RDX—display this pattern of thermal behavior (Figures 1 and 2).

A type of explosive composition quite likely to be encountered in "home-made" and terrorist devices is a mixture of an oxidizer and a fuel, com-

monly referred to as a pyrotechnic composition. Although usually less explosive in nature than the true "high explosives", these compositions are capable of substantial destructive power when properly prepared and packaged. Pyrotechnic mixtures are normally prepared to produce visual and/or audible effects (e.g., fireworks), but they can be used for explosive purposes if the proper conditions are employed.

These mixtures will vary enormously in behavior, depending on the degree of mixing, the particle size of the ingredients, and the degree of confinement of the composition upon ignition. High confinement (e.g., powder loaded in a metal pipe) accelerates the burning process and can lead to an explosion for a mixture that will merely burn vigorously if ignited in the open. The ingredients commonly encountered in such mixtures include:

1. Oxidizers—Oxygen-rich compounds such as potassium chlorate ( $\text{KClO}_3$ ) and potassium nitrate ( $\text{KNO}_3$ ).
2. Fuels—Readily-oxidized materials that react with the oxidizer to produce heat and gas.

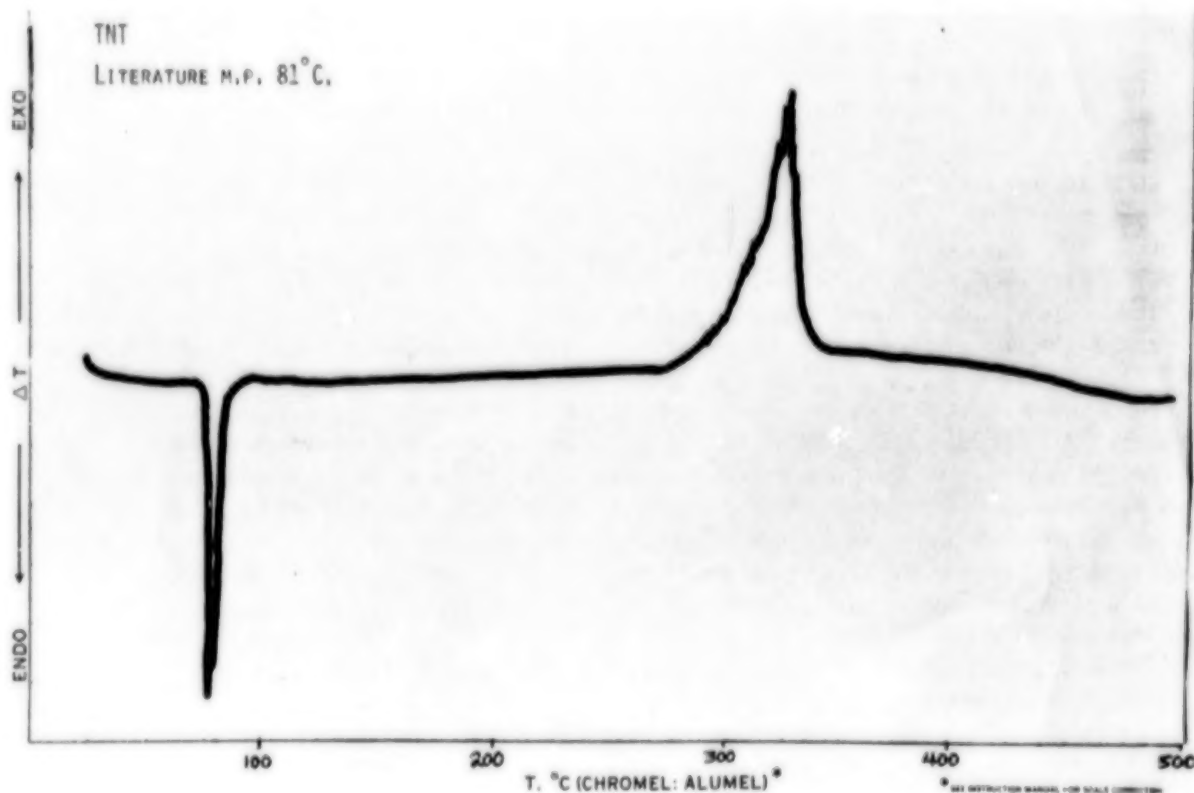


Figure 1. Thermogram of pure TNT. An endotherm is observed for the melting point near 81°C. A broad exotherm associated with decomposition can be seen at 300–330°C.

Examples are Mg, Al, charcoal, and organic compounds such as sugar.

3. Binder—Polymeric material added to blend the components together. The binder can also act as an extra fuel.

In commercial pyrotechnic mixtures, other ingredients are added to produce colored flames, smoke, burning rate control, and storage stability.

These compositions can be quite exothermic upon ignition. Some representative enthalpy values are given in Table 1. As a comparison, TNT has a heat of explosion of 0.93 cal/gram.

**Table 1. TYPICAL HEATS OF REACTION FOR PYROTECHNIC MIXTURES**

Composition (% by weight)	Heat of Reaction (Kcal/gram)
KClO <sub>4</sub>	66
Al	34
KClO <sub>4</sub>	60
Mg	40
Fe <sub>2</sub> O <sub>3</sub>	75
Al	25
KNO <sub>3</sub>	75
C	15
S	10
KClO <sub>3</sub>	35
Lactose	25
Rhodamine (Dye)	40

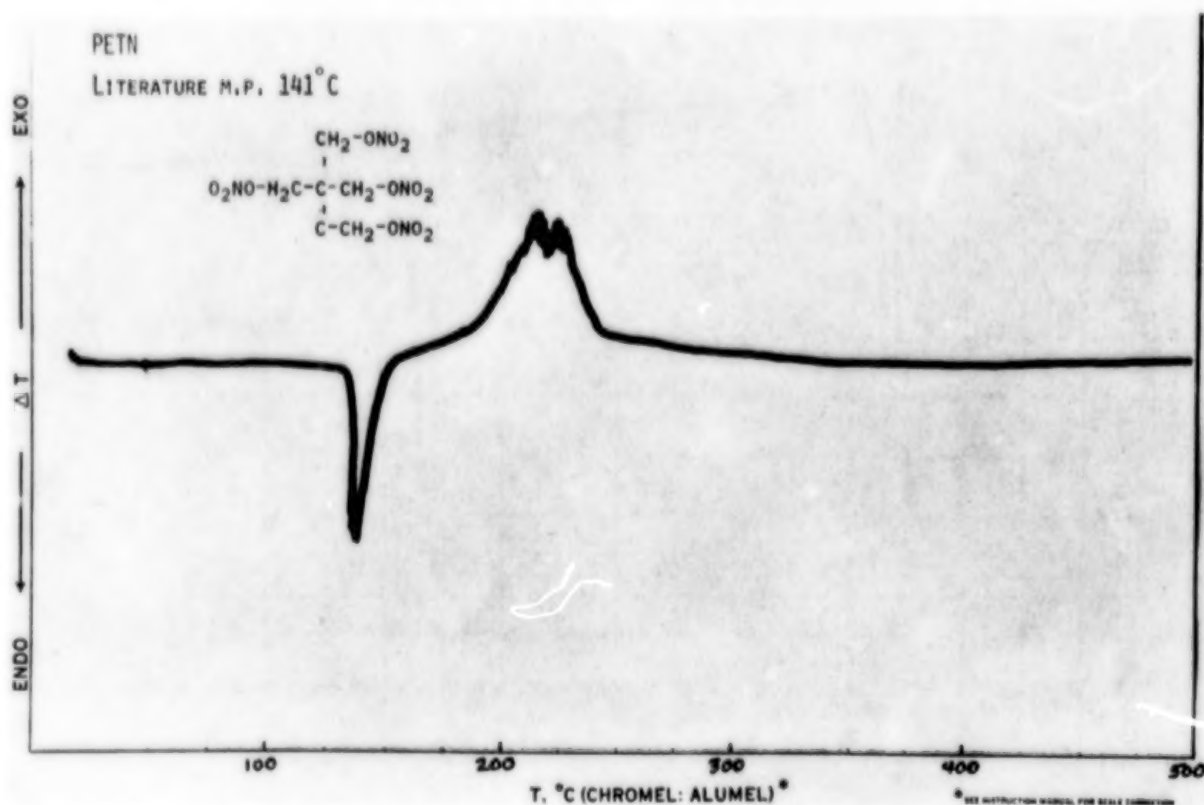


Figure 2. Thermogram of pure PETN. A sharp melting point endotherm occurs near 140°, followed by exothermic decomposition above 200°C.

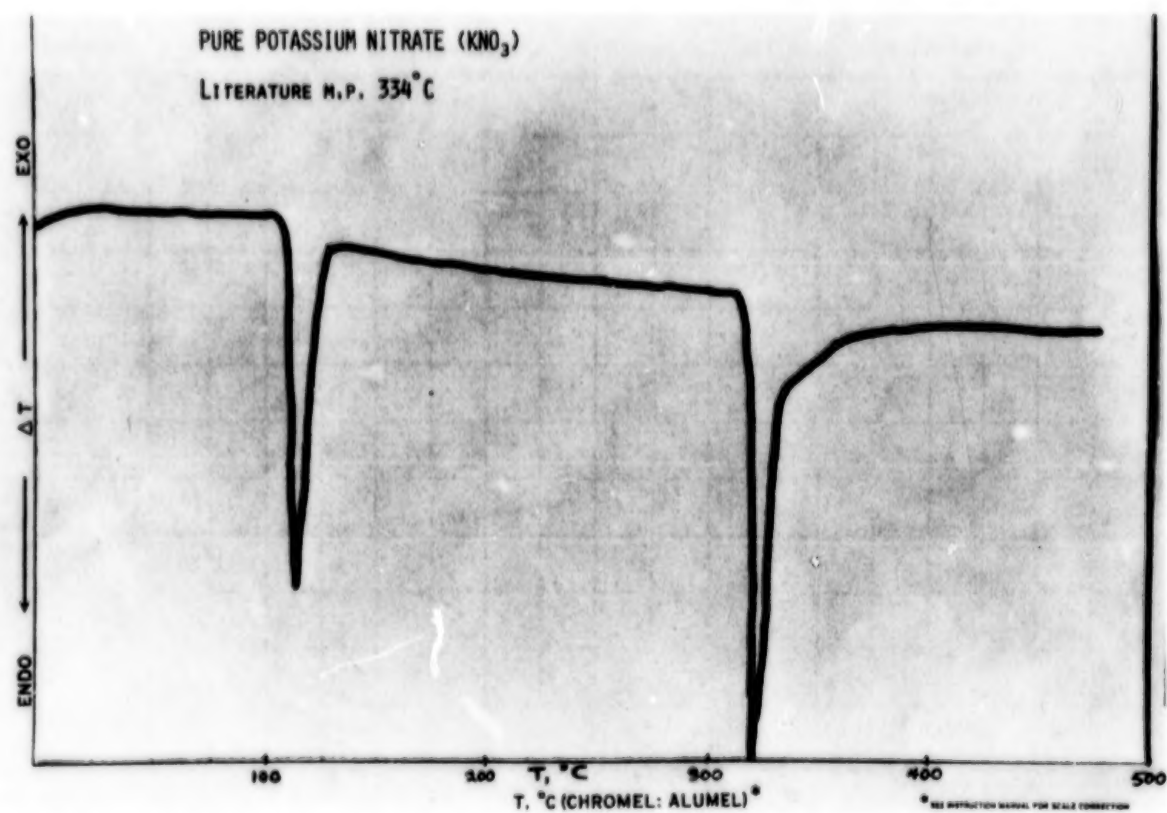


Figure 3. Pure potassium nitrate. This thermogram shows a sharp endotherm for the rhombic-to-trigonal crystalline phase transition near  $130^\circ\text{C}$ , and an endotherm for melting at  $334^\circ\text{C}$ .

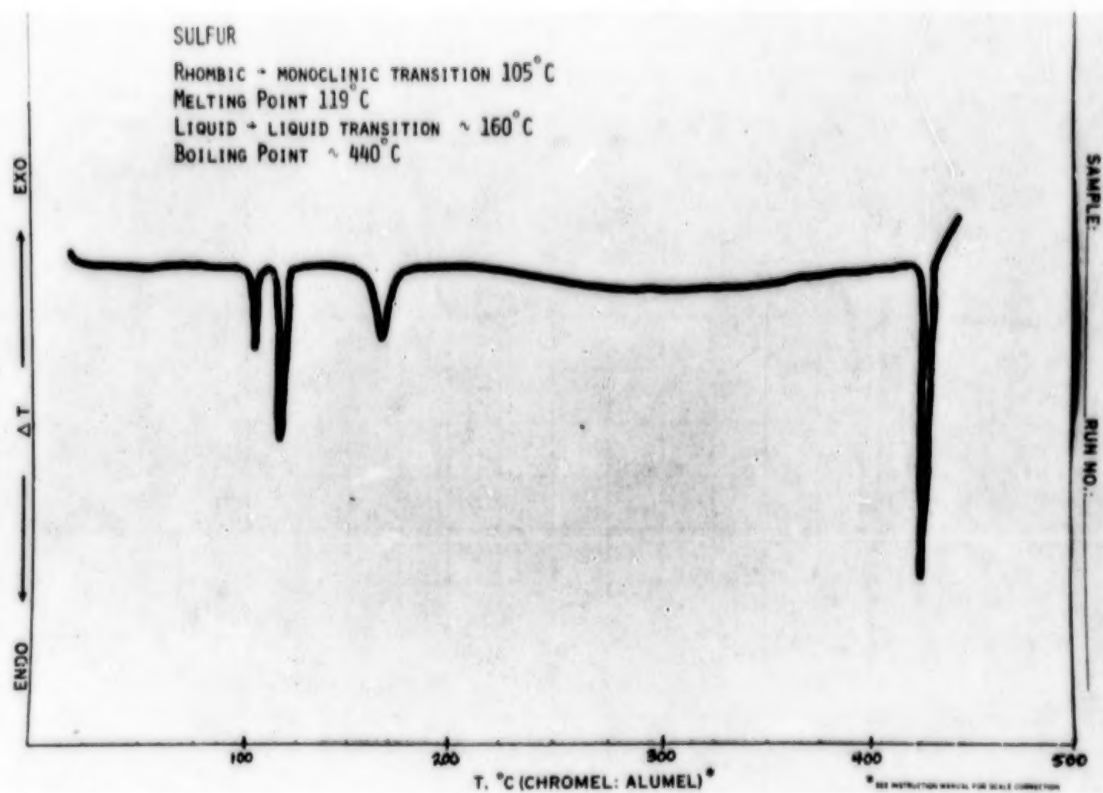


Figure 4. Sulfur. Endotherms for a rhombic-to-monoclinic crystalline phase transition and melting are seen at  $105^{\circ}\text{C}$  and  $119^{\circ}\text{C}$ , respectively. An additional endotherm is observed near  $170^{\circ}$ . This peak corresponds to the fragmentation, in the liquid state, of 8-member sulfur rings into smaller units. Finally, an endotherm for vaporization is seen near  $440^{\circ}\text{C}$ .

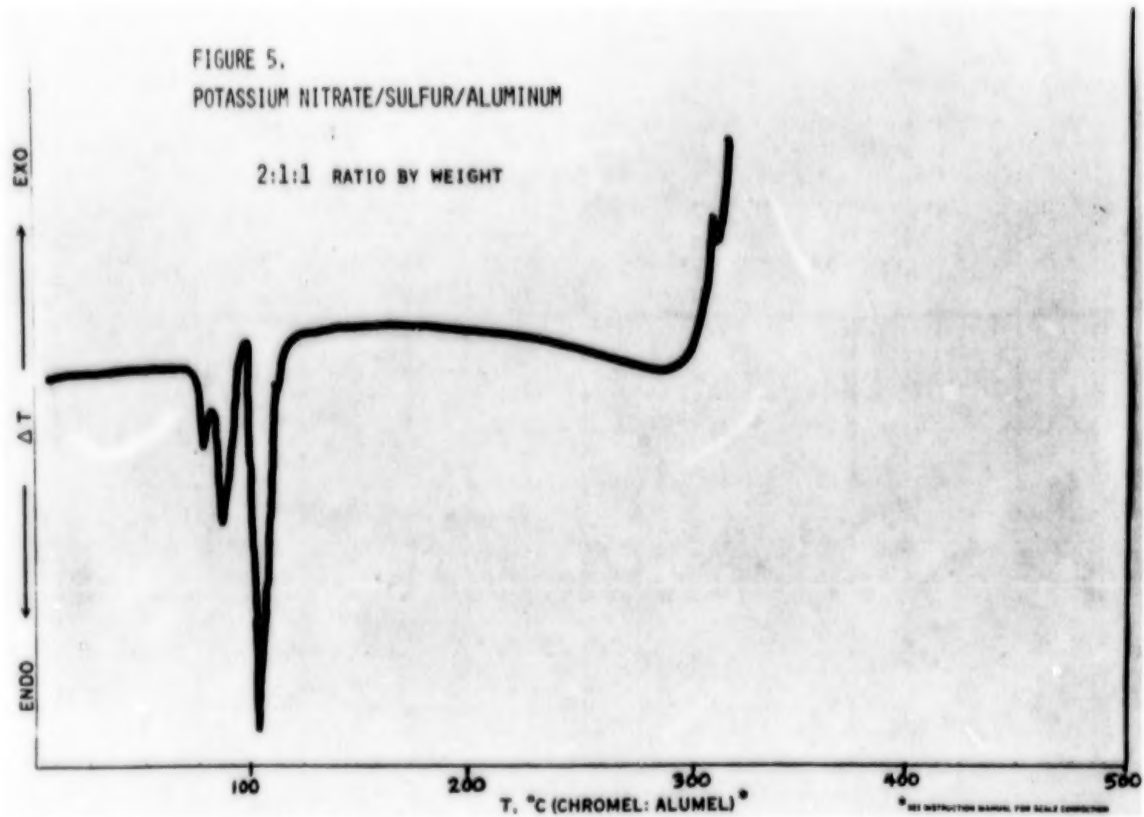


Figure 5.  $\text{KNO}_3/\text{S}/\text{Al}$  Mixture. Endotherms for sulfur can be seen near 105 and 119°C, followed by the phase transition for potassium nitrate at 130°. As the melting point of  $\text{KNO}_3$  is approached (334°C), an *exotherm* is observed. A reaction has occurred between the oxidizer and fuel, and ignition of the composition occurs. Apparently, once the solid lattice of the  $\text{KNO}_3$  breaks down, intimate mixing of oxidizer and fuel can take place and a self-propagating reaction commences.



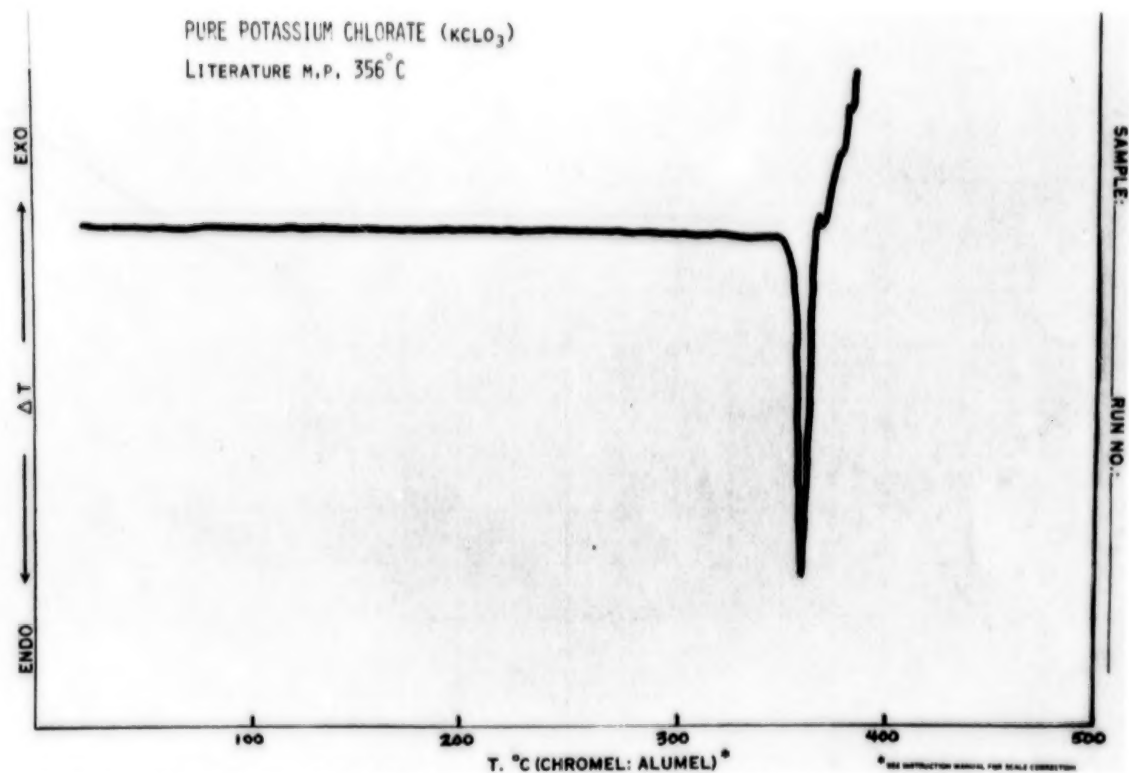


Figure 6. Pure potassium chlorate ( $\text{KClO}_3$ ). No thermal events are observed prior to the melting point near  $356^\circ\text{C}$ . Exothermic decomposition of the compound occurs above the melting point, producing oxygen gas and potassium chloride ( $\text{KCl}$ ).

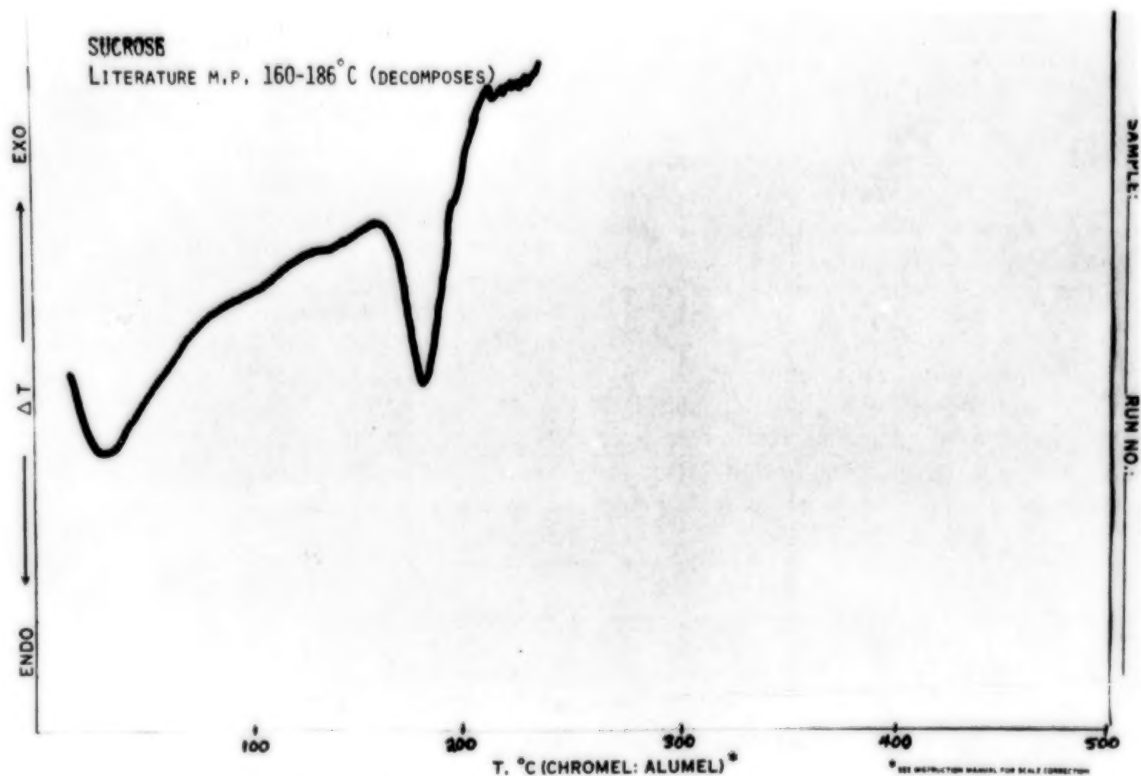


Figure 7. Sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). A broad endotherm is observed commencing near  $160^\circ\text{C}$ . Sucrose decomposes as it melts over the temperature range  $160\text{--}186^\circ\text{C}$ .

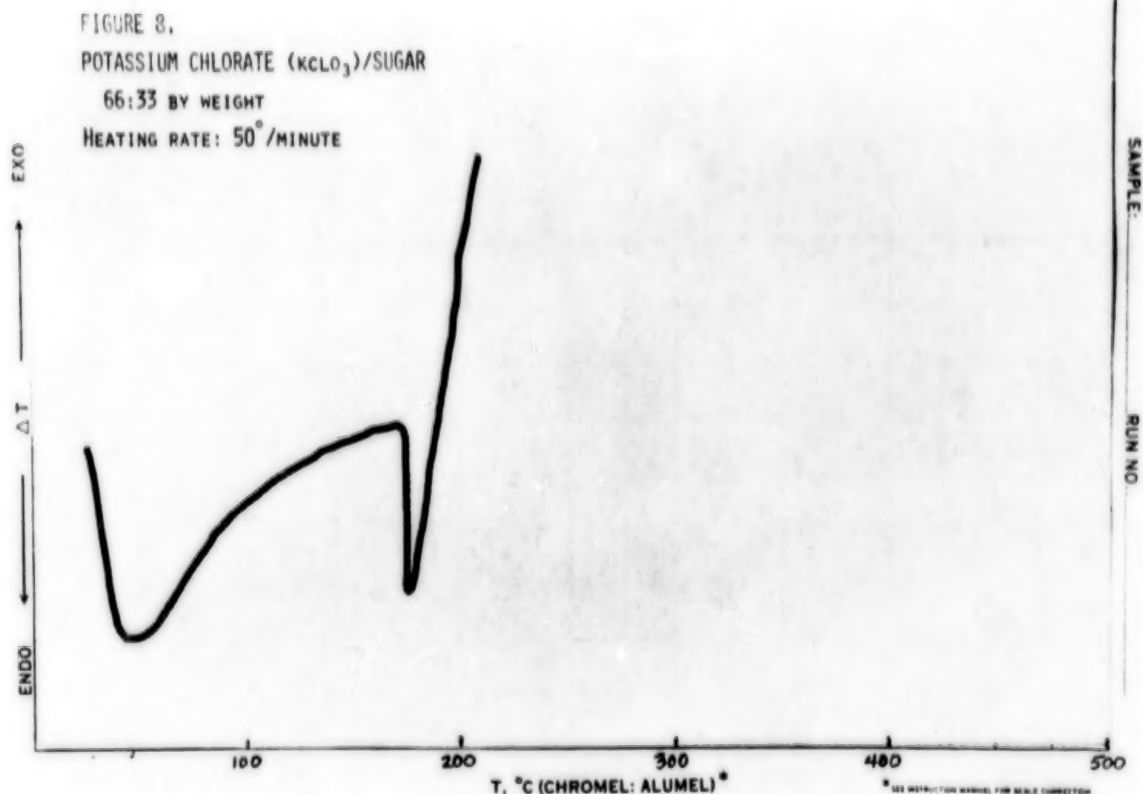


Figure 8.  $\text{KClO}_3$ /Sucrose. A thermal pattern quite similar to that of sucrose is obtained up to 175°. At that point, a violent reaction occurred in the sample tube, expelling the thermocouple. Ignition was observed at the melting point of the fuel. The ignition temperature (180°C) is well below the melting point of the oxidizer (356°C) for this mixture.

#### REFERENCE

Shidlovsky, A. A. Principles of Pyrotechnics (trans. from Russian), Report AD/A001859, Foreign Technology Division, Wright-Patterson Air Force Base, 1974. Available from National Technical Information Service, Springfield, VA.

The thermogram for a pyrotechnic mixture will be a composite of the various components up to the occurrence of an exothermic reaction between the oxidizer and fuel, leading to ignition of the composition. Figures 3-8 illustrate the thermal

patterns typical of oxidizers and oxidizer/fuel mixtures. Note in particular the *Low* ignition temperature of the potassium chlorate/sugar composition. This behavior is typical of  $\text{KClO}_3$ -containing compositions, and indicates why such mixtures are hazardous to manufacture and prone to self-ignite.

Differential thermal analysis can provide a rapid indication of the identity and potential hazard of many unknown compositions, and also can provide valuable data on ignition temperatures. DTA is an instrumental technique that should be a routine part of all laboratory investigations of high-energy materials.

## IDENTIFICATION OF TWO RARE EXPLOSIVES

*Shmuel Zitrin, Shmuel Kraus and Baruch Glattstein*

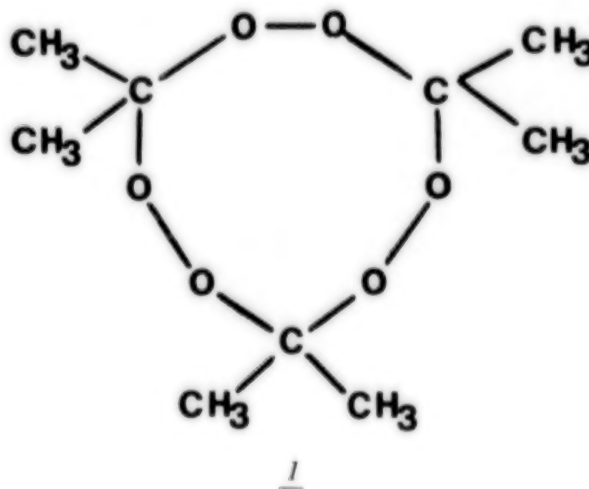
Criminal Identification Division,  
Israel Police Headquarters, Jerusalem, Israel.

**ABSTRACT.** Two unusual and rare explosives were identified in two separate cases of terrorist activity. The two explosives were identified as hexamethylenediamine peroxide and triacetoneperoxide. The identification was based upon interpretation of spectral characteristics of the compounds. These included mass spectrometry under electron impact (EIMS) and chemical ionization (CIMS) conditions, infrared (IR) spectrometry and nuclear magnetic resonance (NMR) spectrometry. The explosives were first identified when no known spectra of them were available in our laboratory library. Their identity was later confirmed by comparison with data from literature; the comparisons included melting points and IR spectra. The two explosives, which are organic peroxides, were described extensively in older literature, but their current use as military explosives has not been reported. Although the explosive properties of the two compounds correspond to those of primary explosives, one of them, triacetoneperoxide, was employed by terrorists as a main charge. Special significance should be given by law enforcement agencies to the simplicity of preparation of the two explosives, as well as to the ready availability of the starting materials needed for their synthesis. In the case of triacetoneperoxide, the preparation was described in the testimony of an apprehended terrorist. An interesting point which could be relevant to the detection of these explosives by X-rays is that contrary to common primary explosives (e.g., lead azide or mercury fulminate), these peroxide explosives contain no metallic elements. Therefore their presence cannot be detected by standard airport security procedures.

Two explosives which had not been previously encountered in our laboratory were identified in cases related to terrorist activity. The two explosives, known as triacetoneperoxide and hexamethylenetriperoxidodiamine (HMTD) are both organic peroxides which were first reported by German chemists in the late nineteenth century. The two explosives arrived at our laboratory as "completely unknown" samples and their identification is described in this paper. In addition, new evidence for their structures is given.

Triacetoneperoxide (TATP, 1) was brought to our laboratory as a white powder found inside a pipe at the site of a terrorist attack in Hebron. It had been intended to be used as a main charge but only a part of it exploded.

The powder, which had explosive properties, was found to be organic by its infra-red (IR) spectrum (Figure 1). The IR spectrum lacked the characteristic absorption bands due to the stretching vi-



brations of the nitro group (1). Our standard thin-layer chromatography (TLC) procedures (2), which have been designed to detect nitro-containing explosives, failed to detect such explosives in

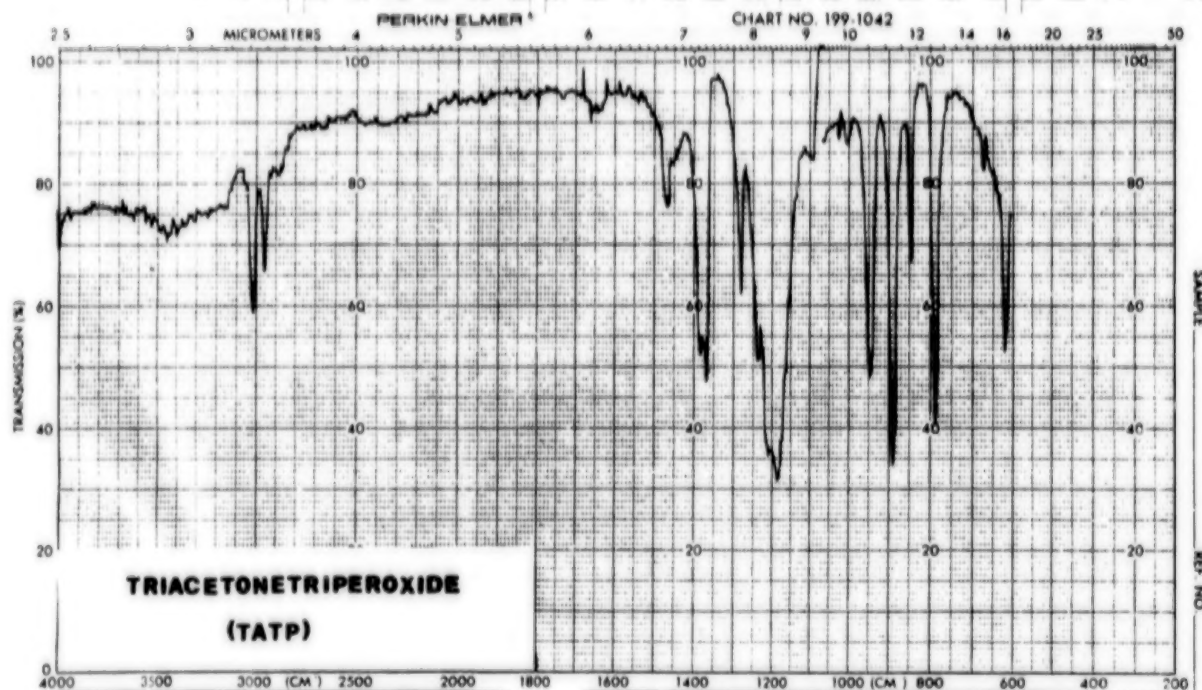


Figure 1. The IR spectrum of TATP (1).

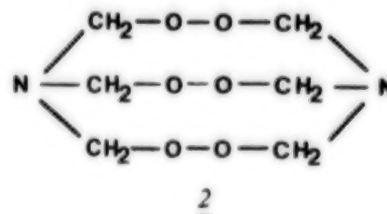
the unknown powder. It was clear from the IR spectrum that the unknown explosive was not aromatic.

Mass spectra were recorded in both chemical ionization (CI) and electron ionization (EI) modes. Most of the ion current in the EI mass spectrum (Figure 2) was concentrated in the relatively uninformative low mass region. The CI mass spectrum (Figure 3), with isobutane as the reagent gas, was much more informative. The distinct ion at  $m/z$  223 could be attributed to the protonated molecule. A series of low abundant ions at  $m/z$  101, 117 and 133 differed by 16  $m/z$  units, corresponding to the mass of an oxygen atom. This was the first clue that a peroxide could be involved. The similarity between parts of the EI mass spectrum (Figure 2) and the EI mass spectrum of acetone was noticed and the following preliminary literature survey (3a) led us to the tentative identification of the unknown powder as TATP. It melted at 92°C, which was close to the melting point of TATP (3a). The IR spectrum (Figure 2) was reexamined and most of its absorption bands were explained by the structure 1 of TATP. The band at 872  $\text{cm}^{-1}$  could be attributed to O-O stretching vibrations in peroxides (4). The IR spectrum matched the previously published spectrum of TATP (5).

The  $^1\text{H}$ -nuclear magnetic resonance (NMR) spectrum showed that all the protons absorbed as a singlet, at a chemical shift ( $\delta$ )  $\sim$  1.47 p.p.m. (in  $\text{CDCl}_3$ ). According to a previous NMR study (6), TATP has chiral molecules and could potentially be resolved into two enantiomers.

TATP or 3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexoxonane was first prepared by Wolfenstein in 1895 (7) by a reaction between acetone and 30%  $\text{H}_2\text{O}_2$  in the presence of an acid. A white crystalline product was obtained; it exploded violently by friction.

Hexamethylenetriperoxidediamine (HMTD, 2) was brought to our laboratory as a white powder from a detonator. The detonator, which was made of plastic instead of metal, was found on a woman crossing a bridge over the Jordan river.



Normal TLC procedures (2) failed to detect nitro-containing explosives in the white powder. The IR spectrum (Figure 4) had no absorption

bands related to nitro groups. It also showed the absence of aromatic compounds.

EI (Figure 5) and CI (Figure 6) mass spectra led to the identification of the powder. A molecular weight of 208 is clearly indicated by the molecular ion in the EI mass spectrum (Figure 5) and by the  $[M+H]^+$  and  $[M+C_4H_9]^+$  ions in the CI-isobutane mass spectrum (Figure 6).

The loss of 32 m/z units from the molecular ion in the EI mass spectrum could indicate a loss of  $O_2$  (although loss of 32 m/z units is usually associated

in mass spectrometry with methanol elimination). An examination of the IR spectrum (Figure 4) indicated the possible presence of an O-O stretching vibration at  $875\text{ cm}^{-1}$  (4). Once the possibility of a peroxide was considered, a literature survey (3b, 8) led to the identification of the powder as HMTD. The powder melted at  $145^\circ\text{C}$ , which was similar to previously reported values (3b, 8).

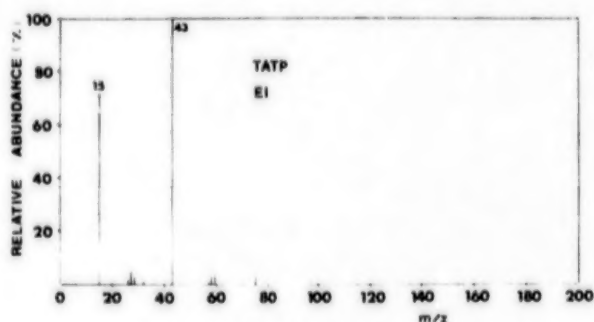


Figure 2. The EI mass spectrum of TATP (1).

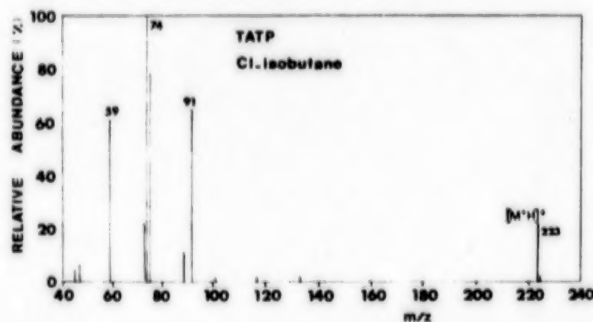


Figure 3. The CI-isobutane mass spectrum of TATP (1).

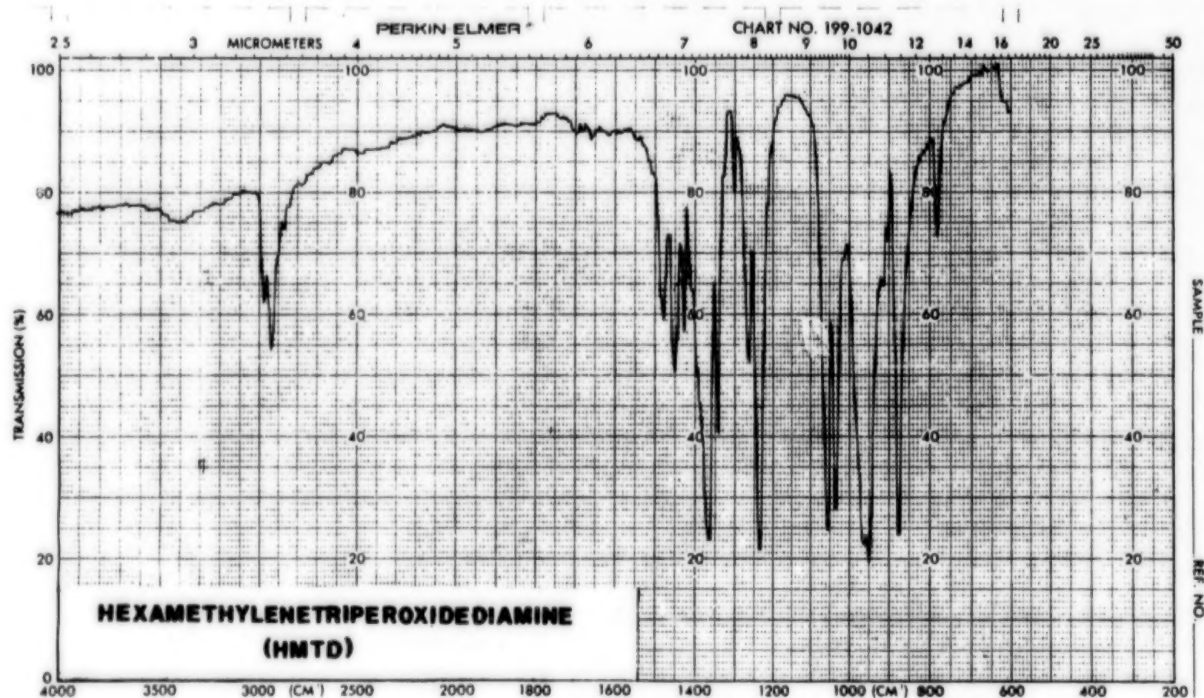


Figure 4. The IR spectrum of HMTD (2).



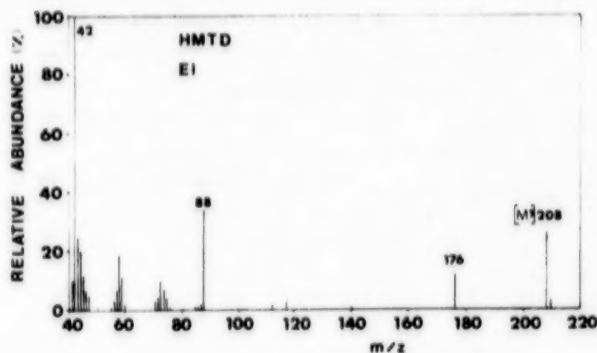


Figure 5. The EI mass spectrum of HMTD (2).

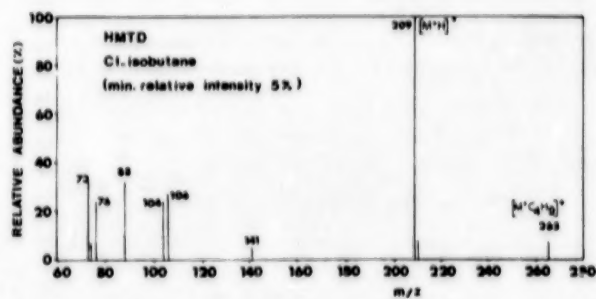
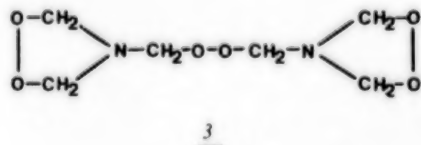


Figure 6. The CI-isobutane mass spectrum of HMTD (2).

When the powder reached its melting point, the capillary tube containing it exploded violently. The fragmentation patterns in the EI (Figure 5) and CI (Figure 6) mass spectra could be rationalized by the structure of HMTD. The IR spectrum (Figure 4) matched a previously reported one (9).

HMTD was first prepared by Legler in 1881 (10) by oxidizing formaldehyde with  $H_2O_2$  and reacting the product with ammonia. The structure 2 was proposed by Baeyer and Villiger in 1900 (11). An alternative structure 3 was proposed by Grisewald and Siegens in 1921 (12).



Both formulae, 2 and 3, were mentioned by Urbanski (8). The chemical abstract nomenclature is based on structure 2: 3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4.4.4] tetradecane, probably following the IR study of Ferroni et al. (9). The mass spectra (Figures 5 and 6) could not differentiate unequivocally between the two structures. The highly abundant ion at  $m/z$  88 in the EI mass spectrum (Figure 5) may result from the molecular ion of 3 by a simple  $\alpha$  cleavage. It may also result from the molecular ion of 2 through an extensive rear-

angement.  $^1H$ -NMR of HMTD points to structure 2: only one type of methylene protons appears at  $\delta \sim 4.7$ , p.p.m. showing an expected AB pattern. As HMTD is insoluble in water or most organic solvents, the NMR spectrum was run in dimethyl sulfoxide- $d_6$  ( $DMSO-d_6$ ).  $^{13}C$ -NMR (in  $DMSO-d_6$ ) also supports structure 2: the carbon atoms resonate as a singlet, at a chemical shift 89.3 p.p.m.

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# IDENTIFICATION AND QUANTITATION OF AN UNKNOWN EXPLOSIVE

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**ABSTRACT** The methodologies employed in the identification, structural determination, and quantitation of the constituents of an unknown explosive mixture will be described. The techniques used include chemical tests, elementary analysis, thin-layer chromatography (TLC), infrared absorption spectrophotometry (IR), ultraviolet-visible absorption spectrophotometry (UV-VIS), nuclear magnetic resonance (NMR), gas chromatography/mass spectrometry (GS/MS), positive and negative ion chemical ionization mass spectrometry (PINICIMS), and high resolution electron impact mass spectrometry (HREIMS). The structural determinations were based primarily on the HREIMS data along with chemical stability considerations, the molecular weight and the structural data derived from PINICIMS, NMR, and IR. The positive identification of the unknown was made by synthesizing the compound and comparing its characteristics with those of the unknown in question by various instrumental techniques. Both NMR and HPLC were used in the composition analysis.

## INTRODUCTION

Recently, this Laboratory was involved in the difficult task of analyzing an unknown liquid explosive mixture which had never been encountered. In this paper, the methodologies employed for the identification, structural determination, and quantitation of the constituents in the mixture, together with part of the experimental results, will be described.

## INITIAL RESULTS

The unknown explosive was a clear, pale yellow, viscous liquid with a pungent odor. Various techniques were initially used to identify the unknown. These included chemical tests, microscopic observations, elemental analysis, thin-layer chromatography (TLC), high performance liquid chromatography (HPLC), infrared absorption spectrophotometry (IR), ultraviolet-visible absorption spectrophotometry (UV-VIS), proton nuclear magnetic resonance (NMR), gas chromatography/electron impact mass spectrometry (GC/EIMS), and direct-inlet probe mass spectrometry (DIPMS).

Figures 1, 2, and 3 show, respectively, the repre-

sentative mass spectra for the low-, medium-, and high-boiling fractions of the sample with  $m/e$  of 43, 137, and 185 as the respective base peaks. These three distinctly different mass spectra were obtained during repetitive scanning of samples by DIPMS. During this experiment, which used essentially a crude MS/MS technique, the sample was heated slowly from ambient temperature to about 300°C and the spectrum scan continued until no useful spectrum could be obtained. These

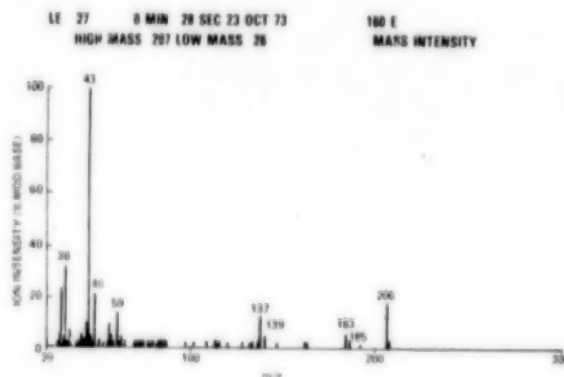


Figure 1. Mass Spectrum of Low-Boiling Fraction of Unknown Explosive

(Scan No. 27; Scan Time 28 Sec)

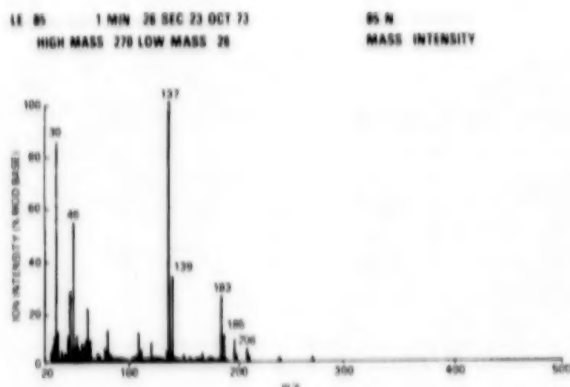


Figure 2. Mass Spectrum of Middle-Boiling Fraction of Unknown Explosive

(Scan No. 85; Scan Time 86 Sec)

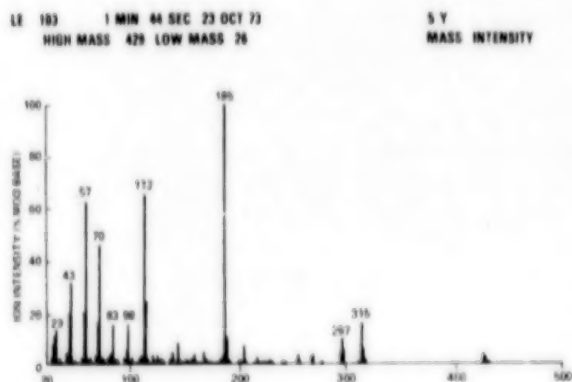


Figure 3. Mass Spectrum of High-Boiling Fraction of Unknown Explosive

(Scan No. 103; Scan Time 104 Sec)

spectra revealed the following: (1) the unknown explosive was a multicomponent mixture; (2) it was nonaromatic; (3) it contained at least one chlorine atom ( $m/e$  137, 139, and 183, 185 with intensity ratios of 3 to 1)  $\text{NO}_2$  group(s) ( $m/e$  46 and 30), and possibly, a  $\text{CH}_3\text{CO}$  group ( $m/e$  43); and (4) the molecular weights of the constituents were at least 200.

Figure 4 shows a reconstructed ion chromatogram (RIC) obtained in the GC/MS experiment.

Peaks 86 and 762 are solvent and column contamination, respectively. The peak shapes near Scan No. 529 suggested the possible presence of labile component(s) in the unknown.

Figure 5 depicts high performance liquid chromatograms of the unknown.

The results obtained by DIPMS, GC/MS, and HPLC indicated the presence of more than three compounds in the sample. Thin layer chromatography was also employed in an attempt to separate various constituents of the unknown. How-

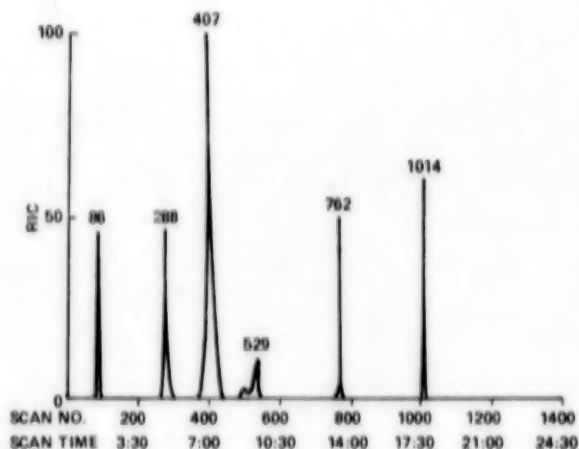


Figure 4. Reconstructed Ion Chromatogram of Unknown Explosive

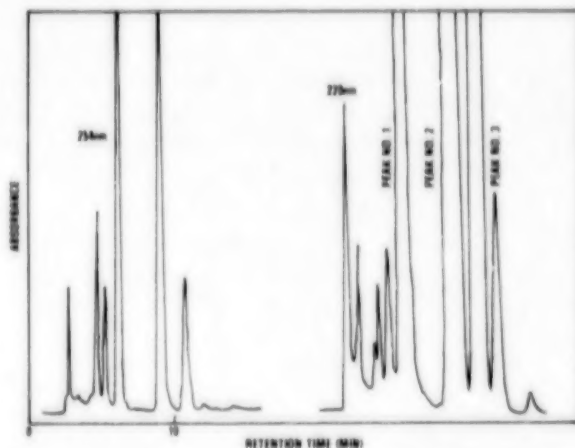


Figure 5. High Performance Liquid Chromatograms of Unknown Explosive

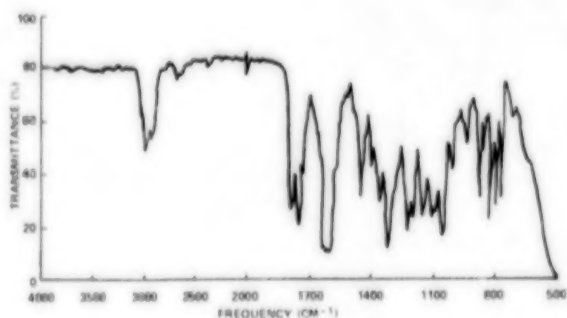


Figure 6. Infrared Spectrum of Unknown Explosive

ever, even with the use of high performance TLC plates, only partial separation was achieved. This was demonstrated in the analysis of the extracts obtained from various zones of the developed plate by DIPMS in the "crude MS/MS" mode described earlier.

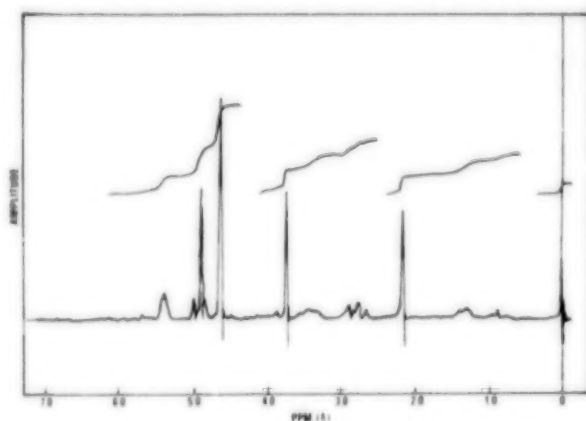
Figure 6 shows the infrared spectrum of a neat

sample of the unknown. The absorption frequencies and the possible group assignments are summarized in Table 1. It should be noted that the IR group assignments were difficult due to the strong influence of other structural features of the compounds on the absorption frequencies.

**Table 1. INFRARED ABSORPTION FREQUENCIES OF UNKNOWN EXPLOSIVE AND POSSIBLE GROUP ASSIGNMENTS**

Legend: S = strong; M = medium; and W = weak	
Absorption Frequencies, $\text{cm}^{-1}$	Possible Group Assignments
3000 (W), 2960 (W), 2920 (W)	Alkane
1777 (S), 1742 (S)	Ester
1600 (S), 1440 (M), 1390 (W), 1340 (W)	R-NO <sub>2</sub>
1310 (S), 1210 (S), 1130 (M), 1080 (M)	—
1040 (M), 1000 (W), 920 (W), 855 (M)	—
820 (M), 800 (M), 780 (M)	—

In Figure 7, the 60 MHz proton nuclear magnetic resonance spectrum is shown. The chemical shifts and the possible group assignments are summarized in Table 2. The observed chemical shifts clearly ruled out the presence of nitroaromatic compounds as well as nitramines. Furthermore, the lack of hydrogen coupling indicated that the compounds in the unknown mixture exhibited high degrees of symmetry. These observations played an important role in the ultimate structural determinations. The unknown sample exhibited strong absorption in the 200 to 240 nm range, the absorbance being the strongest at 200 nm, which is the low cut-off wavelength of the instrument used. The maximum absorption wavelength was, therefore, likely to be located near 200 nm or in the vacuum ultraviolet region. The observed absorption range coincided with those of polynitro compounds such as nitramines. Aside from this useful



**Figure 7. 60 MHz Proton Nuclear Magnetic Resonance Spectrum of Unknown Explosive**

information, however, UV absorption spectra provided little additional insight into the identities of the unknowns.

**Table 2. CHEMICAL SHIFTS OF 60 MHz PROTON NUCLEAR MAGNETIC RESONANCE OF UNKNOWN EXPLOSIVES AND POSSIBLE GROUP ASSIGNMENTS**

Legend: S = singlet; T = triplet	
Chemical Shift ( $\delta$ , ppm)	Possible Group Assignment
5.35 (S), 5.2 (S)	—
4.9 (S), 4.6 (S)	—
3.75 (S)	-O-CH <sub>3</sub>
3.35 (T), 2.7 (T)	O <sup>-</sup>
2.1 (S)	-C-CH <sub>3</sub>

Various chemical tests were also carried out, the most significant observation being the pronounced effect of treatment with aqueous, alkaline solution on the IR spectrum of the sample. The absorptions near  $1700 \text{ cm}^{-1}$  were greatly reduced, indicating the presence of ester linkages, which apparently hydrolyzed under this treatment.

Only cursory examinations of the unknown were made by fast atom bombardment mass spectrometry (FABMS) and Fourier transform mass spectrometry (FTMS). These experiments were performed during demonstrations of these instruments which had just been introduced into the commercial market. Due to the very limited nature of the experiments, no useful information could be extracted from the data obtained.

Attempts were then made to match the existing spectroscopic and chromatographic data files, in particular, the EIMS files of known explosives with the experimental data. However, these efforts were not successful. Peak No. 762, the column contaminant, and Peak No. 1014 were identified to be methyl stearate and di (2-ethylhexyl) sebacate, a plasticizer, respectively.

At this point, all experimental evidence indicated that the explosive constituents of the unknown consisted of nitroaliphatic compounds which were not in common use.

## STRUCTURAL DETERMINATION

Although considerable structural information was obtained in the preliminary studies, especially by GC/EIMS, the lack of molecular weight information hampered the structural elucidation. This information is especially important for the type of compounds under investigation which produce



primarily small fragment ions under the conditions of EIMS. Additional experiments were, therefore, conducted to obtain this necessary information as well as other data crucial to the structural determinations. The methodologies employed will be described in this section. Of the methodologies used, DIP high resolution (HR) EIMS ranked as the most powerful since this technique provided unequivocal data regarding the exact elemental compositions of fragment ions as well as the structural data essential for the structural elucidation of the unknown compounds. Next to HREIMS in usefulness were DIP positive ion chemical ionization (PICI) MS and negative ion chemical ionization (NICI) MS from which key molecular weight information was deduced. Closely ranking behind these two techniques in usefulness were GC/EIMS and GC/PICIMS which permitted rapid separation and characterization of nonlabile constituents of the unknown explosive. These techniques were extremely sensitive and required only minute quantities of samples for analyses. Although not as sophisticated and powerful as various versions of GC/MS, DIPEIMS operated in the "crude MS/MS" mode was capable of generating useful structural data. Aside from these powerful MS techniques, NMR and IR, the former, in particular, provided supplementary structural data which facilitated the identification of the unknowns. The lower sensitivities of NMR and IR, however, limited their usefulness. Preparative HPLC played an important role in providing required quantities of the constituents of the unknown explosive for various structural studies. The advantage of HPLC laid in its ability to isolate nonvolatile and labile species without causing degradation.

#### **Isolation of Pure Components**

Preparative HPLC was used to isolate sufficient quantities of pure explosive components needed for structural determinations and confirmations by MS, NMR, IR, UV, and HPLC. This was accomplished by multiple injections of concentrated explosive sample solutions into the analytical HPLC column under normal phase operations and multiple successive collections of Peaks No. 1 to No. 3 (see Figure 5) fractions. The collected fractions were then freeze-dried to isolate the pure components. Freeze-drying was employed to insure the recovery of volatile and labile components. The procedure used permitted the collection of pure materials directly into 1 mL graduated

concentration tubes. Peak No. 1 was later found to be a mixture of two compounds. However, no further separation was required to determine their structures.

#### **Determination of Empirical Formulas of Fragment Ions**

Accurate mass assignments to  $\pm 6$  millimass units of fragment ions were carried out by DIPHREIMS using both the neat mixture and the pure isolated components. This enabled the determinations of empirical formulas for fragment ions which could be assigned to various fragmentation patterns obtained by GC/EIMS even in the case of a mixture.

#### **Determination of the Molecular Weights of Explosive Constituents**

The pseudo-molecular ions of explosive constituents were obtained by DIPPICIMS using the separated components, with water as the reagent gas and also by GC/PICIMS with methane as the reagent gas. From the structural information obtained by HREIMS and other techniques, the molecular weights of the explosive constituents were deduced from the pseudo-molecular ions. It should be pointed out that the correct molecular weight assignments were often complicated by the lack of data for interpreting the unknown CIMS spectra. Moreover, both PICIMS and NICIMS spectra were found to be essential in the molecular weight determination.

#### **Structural Elucidations**

This represented the most difficult and interesting part of this work. The general approach was to arrive at the most probable structure by taking into consideration primarily the HREIMS data and the molecular weight, together with other structural data derived from PINICIMS, NMR, and IR. In addition, the chemical stability of the proposed structure was carefully considered. This included a literature search on the proposed structure and similar types of compounds. The main problem encountered in this work was to determine the structural features missing in both EIMS and CIMS spectra. For example, in Figure 8, very little structural information was available between  $m/e$  of 131, the largest fragment ion observed in EIMS, and 224, the pseudo-molecular ion of Peak No. 288 obtained by PICIMS. In two other cases, the information gaps amounted to approximately 50% of the molecular structures. This problem arose of course, from the fact that CIMS pri-



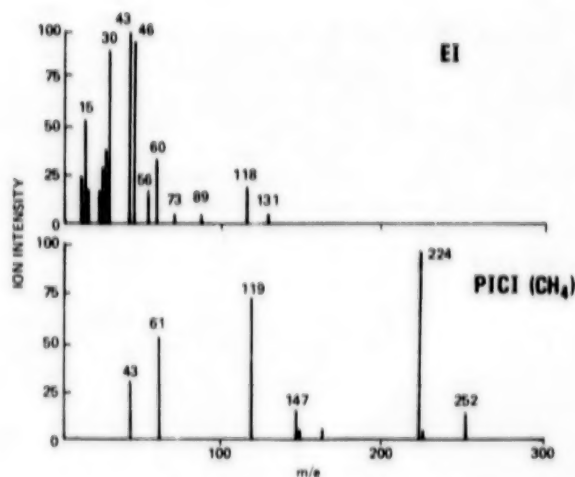


Figure 8. Mass Spectra of Peak No. 288

marily provided pseudo-molecular ion information whereas EIMS of explosive compounds in question gave rise to small fragment ions. Nuclear magnetic resonance and a knowledge of chemical stability played important roles in filling these gaps.

#### Structural Confirmation

This was accomplished by synthesizing the compound and comparing its spectroscopic and chromatographic characteristics with those of the unknown in question by EIMS, NMR, IR, UV, and HPLC.

#### COMPOSITION ANALYSIS

The composition of the unknown explosive was determined by HPLC and NMR. In the case of HPLC, synthetic external standards were employed. One component had to be determined by difference due to the lack of a pure standard. Using NMR, the integrated areas were used in the composition analysis and no standards were needed. Both methods, which are independent, gave essentially identical results.

#### SUMMARY

The methodologies employed in the identification, structural determination, and quantitation of the constituents of an unknown explosive mixture have been described. The techniques used included chemical tests, elemental analysis, TLC, IR, UV-VIS, NMR, GC/MS, PINICIMS, and HREIMS.

The structural determinations were based primarily on the HREIMS data along with chemical stability considerations, the molecular weight, and the structural data derived from PINICIMS, NMR, and IR. The positive identification of the unknown was achieved by synthesizing the suspected compounds and comparing their characteristics with those of the unknowns in question by various instrumental techniques. Both NMR and HPLC were used in the composition analysis.

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## ANALYSIS OF AN UNUSUAL EXPLOSIVE: METHODS USED AND CONCLUSIONS DRAWN FROM TWO CASES

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**ABSTRACT.** Samples of explosive material are often submitted to the FBI Laboratory for identification. In most cases, the sample is quickly identified by Gas Chromatography/Mass Spectrometry analysis and, if a sufficient quantity of pure substance is available, by Infrared Spectroscopy. The resulting spectra are compared with library spectra or spectra obtained from known samples in the laboratory. When no matching spectra can be found among these resources, the examiner must deduce the molecular structure of the material by using fundamental chemical knowledge and by employing whatever appropriate spectroscopic techniques are necessary. The choice of those techniques will depend both on the quantity of material available and on the complexity of the structure. Two recent cases will be discussed with emphasis on the methodologies used by the examiners.

One of the many tasks of the FBI Laboratory is the identification of explosive materials which are linked to criminal activity or threats to national security. Most of the cases are routine; the sample can be analyzed by gas chromatography/mass spectroscopy or infrared spectroscopy and with the aid of a data system, correctly identified within an hour. Occasionally, a sample is encountered where the components have not been seen by any of the personnel in the Laboratory, and the spectra are not recorded in any of the data bases. Such cases force the examiner to use several different types of analytical equipment and piece together the information given by each instrument.

There is no set procedure which will be successful in every case. The tests which are most appropriate for a particular sample depend on the sample quantity and purity as well as the chemical nature of the explosive material itself. The examiner will be constrained by the availability of equipment and the expertise of the personnel in the laboratory.

This paper is about two different explosives which were found in two different cases. These explosives were unusual only in that they had not been seen before by anyone in the FBI and were not present in any of the collections of spectroscopic data available within the laboratory. The lessons learned by the examiners in these cases have led to some changes in the way future cases involving similar materials will be handled.

The first case centered on a sample of white powder which was brought to a FBI field office by an informant who claimed it was new type of high explosive which illegally entered this country. A subsequent investigation established that the powder had originated from a professional chemist who lives in western Europe and had several business dealings with countries in Eastern Europe and the Middle East.

Approximately 2 grams of the powder was sent to the FBI Laboratory for analysis. Initially it was subjected to the tests normally performed on relatively large samples of explosives. Milligram quantities of the powder were found to instantaneously combust when brought within a centimeter of an open flame. The powder was relatively insensitive to shock, and was only slightly soluble in acetone, water, toluene and heptane. Dimethyl sulfoxide proved to be a moderately good solvent for the powder. The sample melted over a range of 149 to 150 degrees Celsius indicating a single component of fairly high purity.

A saturated methylene chloride extract was injected without dilution into a HPLC system which was set up to screen for all the nitrate esters, nitroaromatics and nitramines common to commercial and military explosives. The mobile phase was 60% iso-octane and 40% methylene chloride and the column was 25 cm  $\times$  4.6 mm packed with 5 mm spherical silica. A UV absorption detector set at 254 nm preceded a Thermal Energy Analyzer

(TEA) which was operated with the pyrolysis chamber at 550 degrees Celsius. In this mode the TEA was specific for compounds with  $-N-O$ ,  $O-NO_2$  functional groups. The chromatographic run produced no response on the UV absorbance detector and two very small peaks on the TEA which were consistent with, a few nanograms at most of nitrated material. The two peaks on the TEA trace was interpreted to be impurities in the sample.

Gas chromatography—mass spectroscopy (GC/MS) of the powder proved to be very difficult. No peaks were observed following the solvent peak on the RIC (50–500 M/E) when a methylene chloride extract was injected through a Grob type injector onto a fused silica capillary column coated with cross-linked methyl silicone. A very poorly shaped peak (see Figure 1) did appear on the RIC when the extract was injected with a cold, on-column injector onto a similar column which was directly coupled to the mass spectrometer source. Several runs were made varying the GC and mass spectrometer source conditions to optimize the analysis. The compound would not chromatograph if the oven temperature reached 150 degrees Celsius before elution into the ion source. The electron impact mass spectrum was very dependent on the source temperature and somewhat dependent on the GC interface temperature. Figure 2 represents one of the EI spectrum obtained. The  $M/E = 208$  was interpreted to be  $M+$  and  $M/E = 176$  was apparently loss of  $O_2$ . The loss of methanol was not ruled out but was thought unlikely because no evidence of loss of  $-CH_3$  or  $-OH$  was apparent. The absence of  $M/E$  46 or 30 confirmed the conclusion drawn from the earlier HPLC run that the explosive was not a nitrate ester. The ratio of the 209/208 was .06 indicating 6 carbons in the 208 ion.

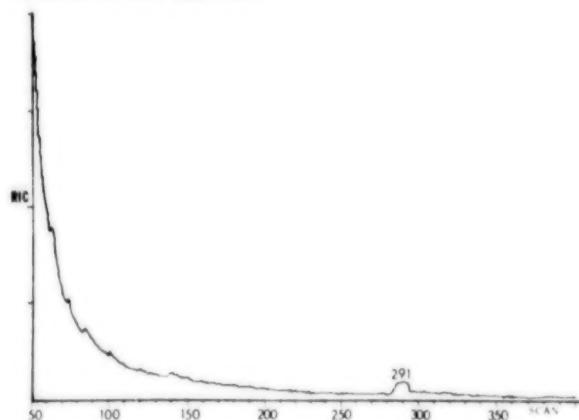


Figure 1. Total ion chromatograph of unknown explosive

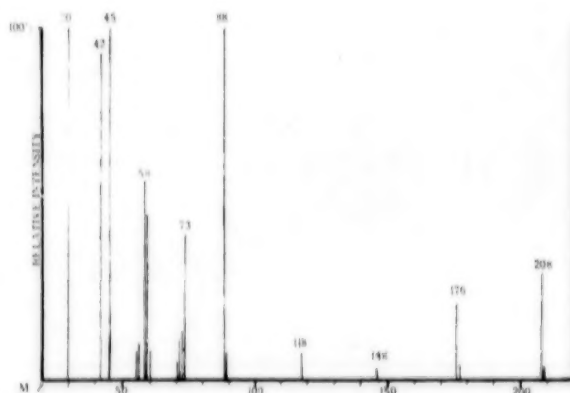


Figure 2. Electron impact (70eV) mass spectra of unknown explosive powder

Chemical ionization GC/MS using .22 torr (indicated) methane and a source temperature of 250 degrees Celsius resulted in the mass spectrum shown in figure 3. The ion at  $M/E = 209$  was interpreted as  $(M+1)^+$ , and the ion at  $M/E$  191 was thought to be  $(M+H-H_2O)^+$ . No other ions were assigned in the spectrum, nor were they correlated with the EI mass spectrum.

A KBr pellet was made from the powder after drying over a dessicant overnight and an infrared spectrum was obtained as shown in Figure 4. The bands at  $2970$  and  $2930\text{cm}^{-1}$  were consistent with  $C-H$  stretch. The broad peak at  $1680\text{cm}^{-1}$  was thought to be the key to successfully interpreting the spectra, however, no assignment could be made which was consistent with the rest of the spectra. It was later shown that this band was due to an impurity. With the exception of those bands which could be assigned to a  $C-H$  bond, no other absorption bands were assigned.

X-ray diffraction of the powder produced the pattern shown in Figure 5. That pattern did not match any published patterns on the references

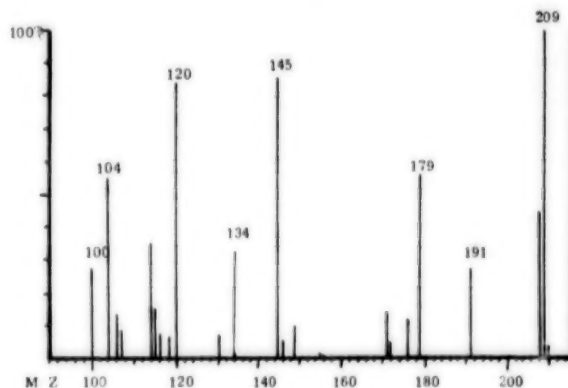


Figure 3. Methane chemical ionization spectrum of unknown explosive powder

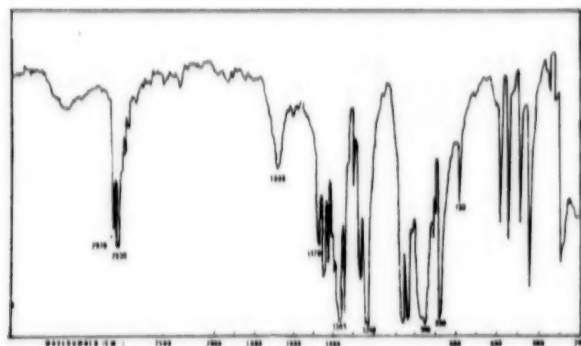


Figure 4. Infrared spectrum of unknown explosive powder (KBr Pellet)

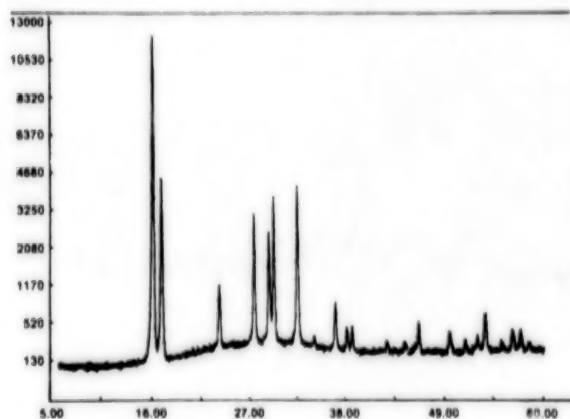


Figure 5. X-ray powder diffractogram

available within the laboratory, but was quite helpful because it indicated a crystal structure of high symmetry.

At this point there was little else that could be accomplished with the equipment available within the FBI Laboratory. The available information was not sufficient for the scientists on the staff to determine the identity of the explosive.

It was decided to go outside the FBI and request the assistance of FDA-Bureau of Foods. They possessed a high resolution mass spectrometer, and a  $^1\text{H}$  and a  $^{13}\text{C}$  NMR which would prove essential in the structural assignment.

An exact mass was obtained of the nominal  $M/E=+208$  using a VG-Micromass ZAB-2F operated in the positive ion-electron impact mode. The resolution was 5,000 and the reference was the 204.9888 ion of perfluorokerosene (PFK). The sample was introduced through the solid probe and heated only by the source which was set at 200 degrees Celsius. The measured exact mass was 208.6695 and the expected error in the measurement was  $\pm 1.0\text{ppm}$ . When the data system was consulted for possible atomic formula with C, H,

N and O, only two possible formula fell within experimental error;  $\text{C}_6\text{H}_{12}\text{O}_6\text{N}_2$  or  $\text{C}_5\text{H}_6\text{O}_1\text{N}_9$ . The second was eliminated as a possibility because of the odd number of nitrogens, which made an even molecular weight unlikely if normal rules of valence were followed. The experiment was repeated using methane chemical ionization and peak matching the  $M/E = +205$  ion of PFK to the  $M/E = +209$  ion. The measured mass was 209.0774 which also was consistent with atomic compositions  $\text{C}_6\text{H}_{13}\text{O}_6\text{N}_2$  corresponding to  $(M + \text{H})^+$ . This data when taken together with the earlier isotopic ratioing experiment performed on the quadripole mass spectrometer strongly indicated that the molecular formula was  $\text{C}_6\text{H}_{12}\text{O}_6\text{N}_2$ .

The  $^1\text{H}$  NMR was obtained from a solution of the powder dissolved in  $d^6$ -DMSO. The spectrum, which appears in Figure 6 shows only a single weak AB system with a chemical shift of 4.3 ppm. The weak AB system was consistent with a molecule having only methylene groups in identical chemical environments. The chemical shift of 4.3 ppm was quite unusual, and was not assigned at that time.

Next, all the spectra were pooled, and structures were drawn until one was found that did not conflict with the data (see Figure 7). The molecule, which is a bicyclic triperoxide with  $D_{3h}$  symmetry, was judged as an unlikely structure by many who viewed it, due to thermodynamic considerations. Consequently a  $^{13}\text{C}$  NMR spectrum of the sample dissolved in  $d^6$ -DMSO was obtained (see Figure 8A). The spectra clearly indicates one carbon with two hydrogens attached. The proton decoupled  $^{13}\text{C}$  NMR spectra shown in Figure 8B further reinforces this interpretation.

With the structural identification verified, a literature search turned up several references to hexamethylenetriperoxide diamine (HMTD). Those references confirmed the solubility and physical data and showed that the potential as a commercial or military explosive was investigated as early as 1904. Those studies concluded that HMTD was too unstable for any commercial application.

The explosive is of interest to forensic scientists, however, because of the obvious utility of HMTD for an unsophisticate terrorist. There are at least two synthesis routes for producing HMTD which require virtually no laboratory equipment and the starting chemicals that can be purchased quite inconspicuously. The explosive can be detonated using the crudest of initiators and has the same deto-

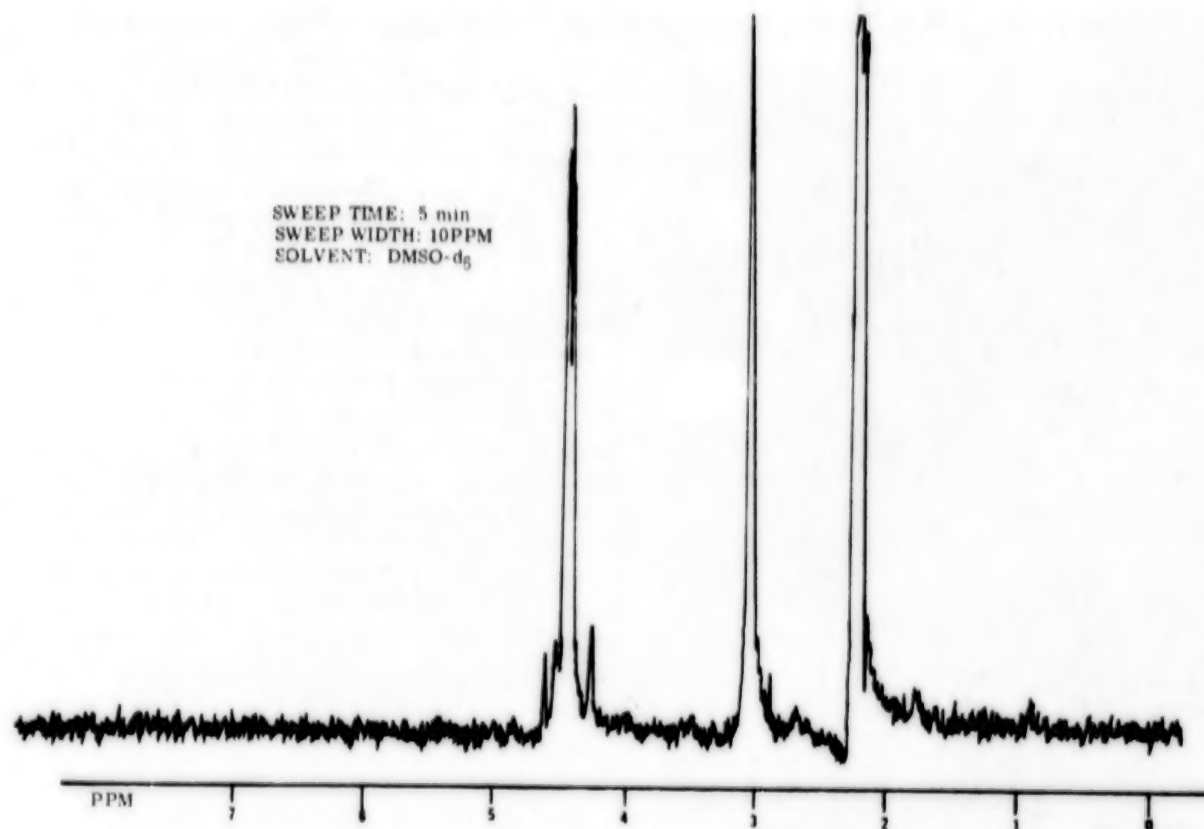


Figure 6. <sup>1</sup>H NMR spectrum of unknown explosive powder

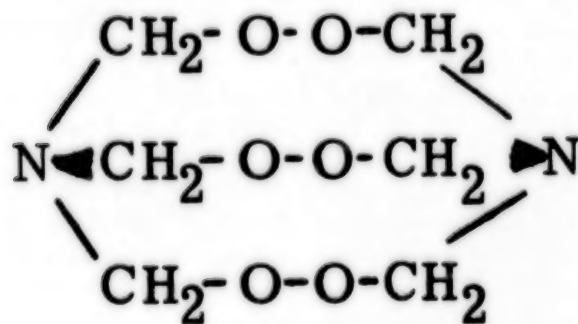


Figure 7. Hexamethylenetriperoxidediamine



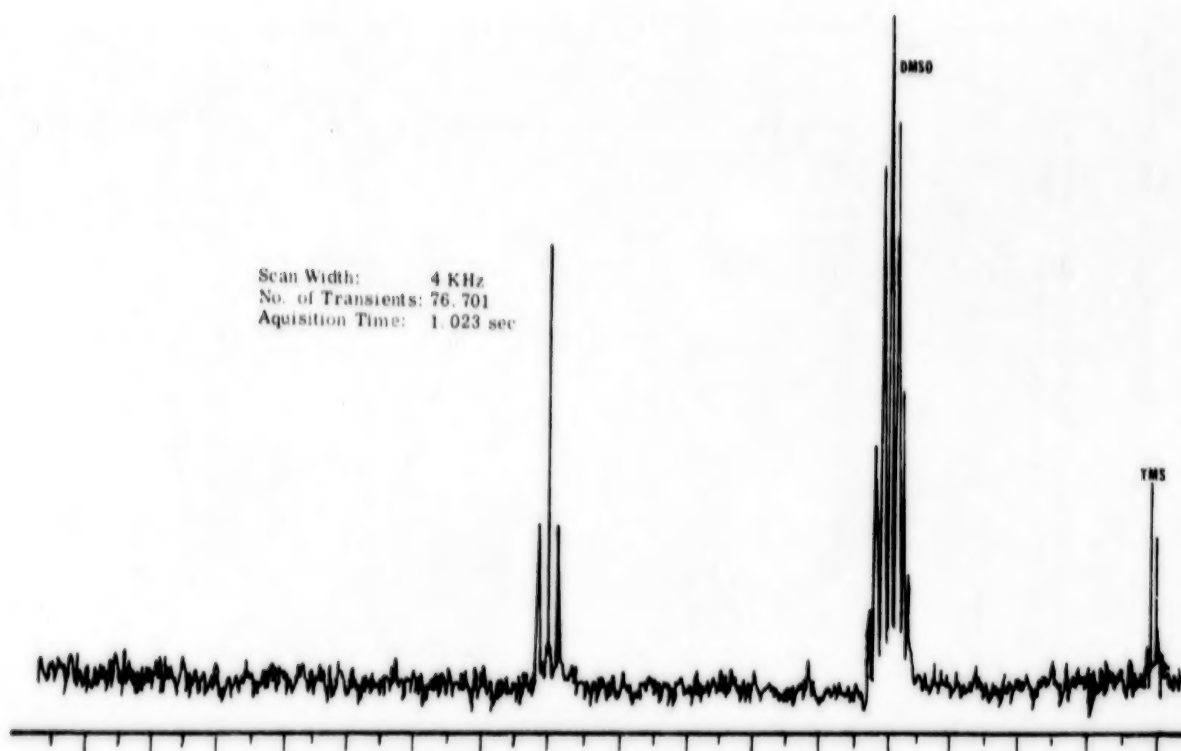


Figure 8-A.  $^{13}\text{C}$  NMR spectrum of unknown explosive powder

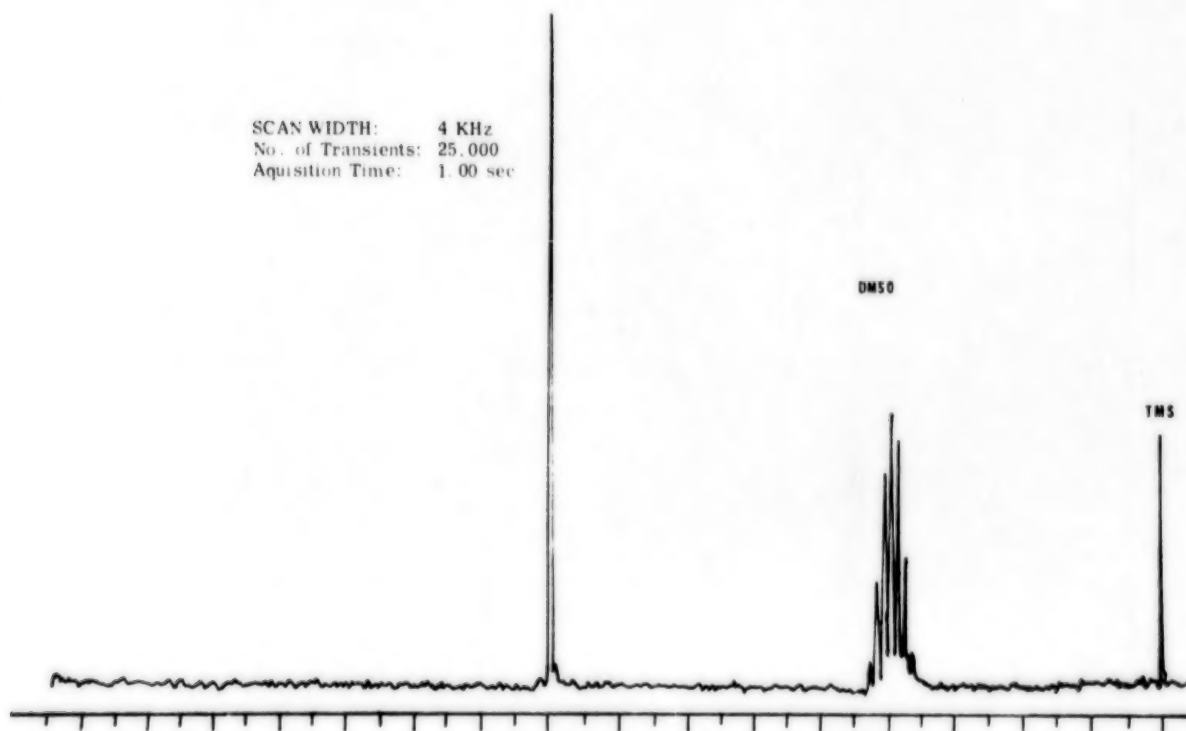


Figure 8-B.  $^{13}\text{C}$  NMR spectrum of unknown explosive powder: protons decoupled

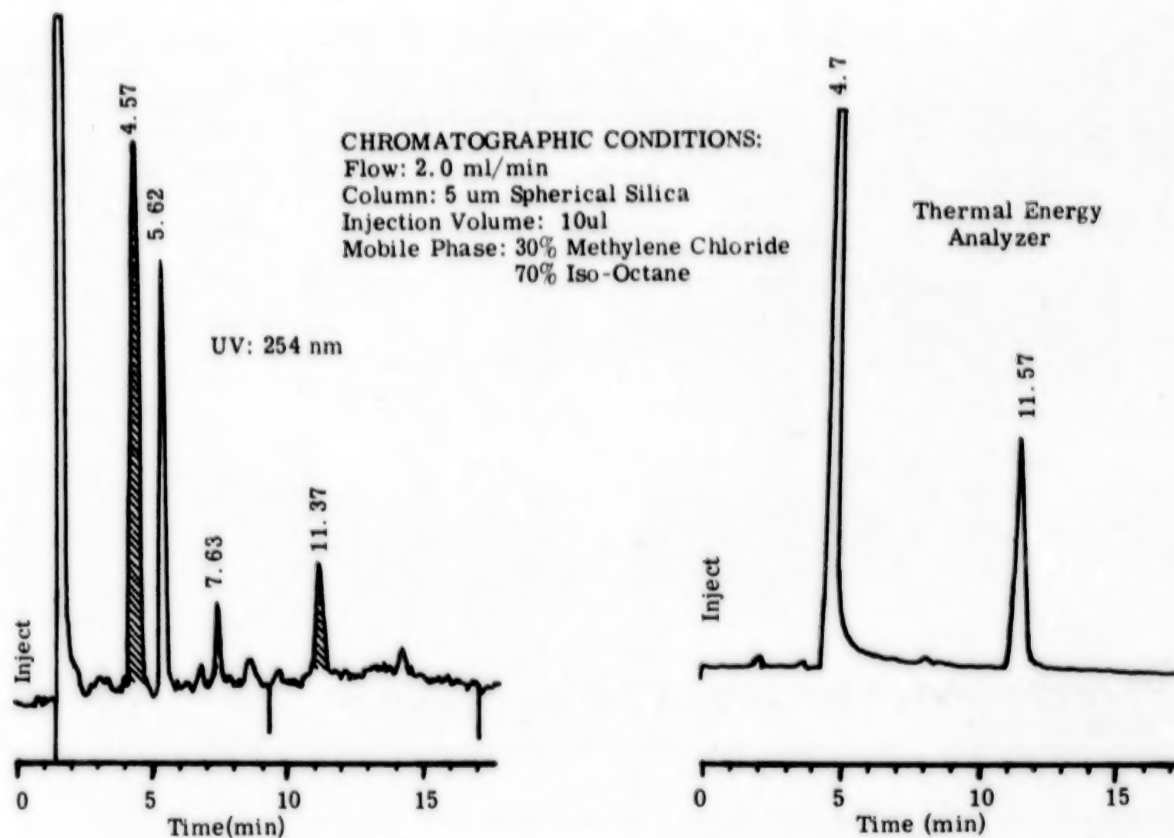


Figure 9. HPLC chromatogram of headspace sample from bombing debris

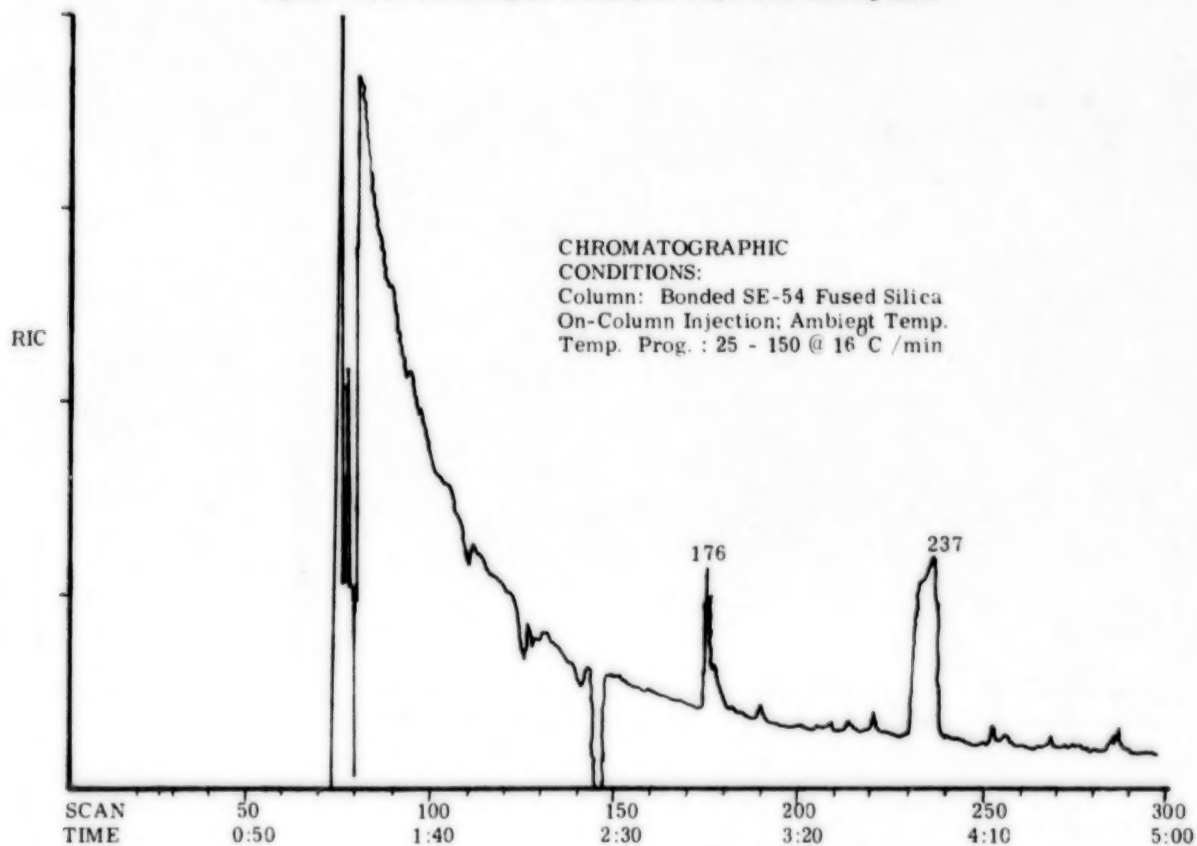


Figure 10. Total ion chromatogram on headspace sample from bombing debris

nation velocity as TNT. The explosive itself is somewhat volatile and all the detonation products are a gas at room temperature.

The second case was a terrorist bombing which occurred outside the contiguous 48 United States which resulted in considerable loss of human life. When the bombing debris reached the FBI Laboratory several pieces of soft material which were obviously near the point of detonation were placed in an air tight can and heated while the vapors of the can were collected on charcoal. After an hour of collection, the charcoal was extracted with methylene chloride. The extract was concentrated with a stream of nitrogen and injected without further preparation into the HPLC system which was described earlier. The trace from the UV detector, which was at maximum sensitivity, showed seven distinct peaks while the TEA showed two very strong peaks (see Figure 9). The retention times did not match those for EGDN, NG, TNT, DNT, PETN, RDX or HMX. The relative responses recorded for the peaks appearing on the two recorders and having the same retention (adjusted for the dead volume between the detectors) were indicative of nitrate esters. The same extract was then analyzed by GC/MS. A cold, on-column injector was used to inject 1  $\mu$ l of the extract onto a fused silica capillary column coated with bonded SE-54. The RIC for the EI GC/MS run is shown in Figure 10. The EI spectra of the first peak which appeared at scan 170 on the RIC appears in Figure 11. The data system searched the EPA-NIH library and found a good match for diethylene-glycol dinitrate (DEGDN). The EI mass spectra for the second component which ap-

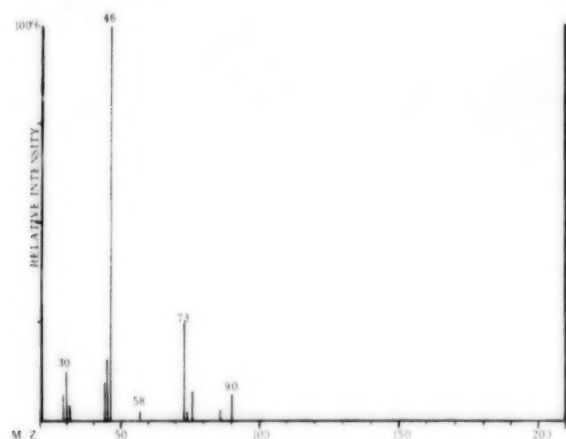


Figure 11. Electron impact (70 eV) mass spectra of first major component of headspace sample from bombing debris

peared at scan 237 on the RIC is shown in Figure 12. That spectrum is indistinguishable from the EI mass spectrum of EGDN, NG and PETN. Another GC/MS run was made using methane chemical ionization and the same GC conditions. The spectra for the first peak was consistent with one that would be expected for a nitrate ester with a molecular weight of 196 daltons, thus reinforcing the tentative identification of DEGDN (see Figure 13). The CI mass spectrum for the second eluting component which is shown in Figure 14 was consistent with a mass spectrum for a nitrate ester with a molecular weight of 255 daltons.

The residue remaining at this point contained approximately 10  $\mu$ g of explosive total, as judged by the response on the HPLC-TEA for other nitrate esters. The possibility of obtaining a useful infrared or NMR spectrum of either component seemed remote. With only DEGDN tentatively identified, identifying the original explosive would be impossible.

The primary use of DEGDN is in propellants, especially some foreign made smokeless powders. The debris, however, was not indicative of smokeless powder damage. The only possibility for identifying the explosive was in identifying the second component found in the headspace. It was decided that the only course left was to go through the available references on explosives page by page to locate a nitrate ester with a molecular weight of 255 daltons. Metriol trinitrate (MTN) emerged as the most likely of the possibilities.

There were no explosives in the FBI collection which contained both MTN and DEGDN. Since the bombing was by a terrorist outside the United States there was a strong possibility that the explosive was foreign made. An expert on foreign manufactured explosives was contacted who identified the most probable source as "Hercudyne," a dynamite made by Hercules in the United States. Arrangements were made to get pure standards of MTN and DEGDN from the manufacturer and those standards were run on the HPLC system and the GC/MS systems for comparison (see Figures 15 and 16). A portion of the bombing debris extract was spiked with the two known explosives and rerun on both HPLC and GC/MS systems. The results of these comparative examinations strongly indicated that the explosive had been identified.

These two cases demonstrated a significant shortcoming of the laboratory procedures used to solve them. All the materials identified in these

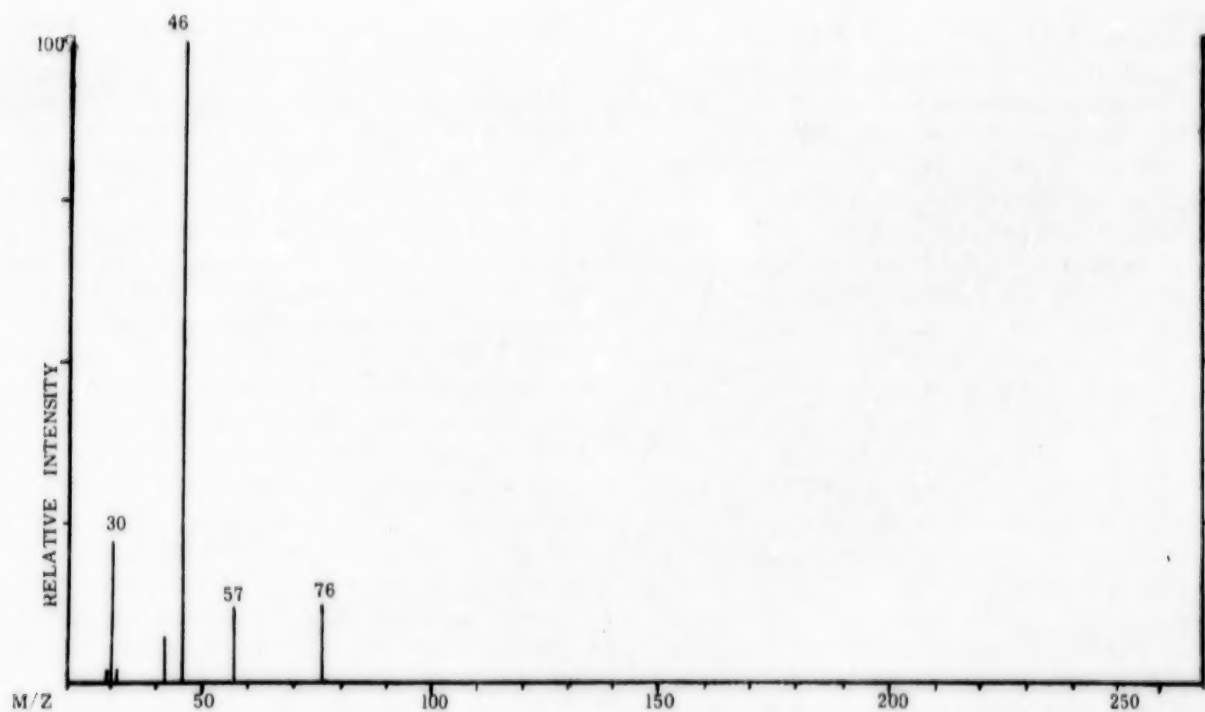


Figure 12. Electron impact (70 eV) mass spectra of second major component of headspace sample from bombing debris

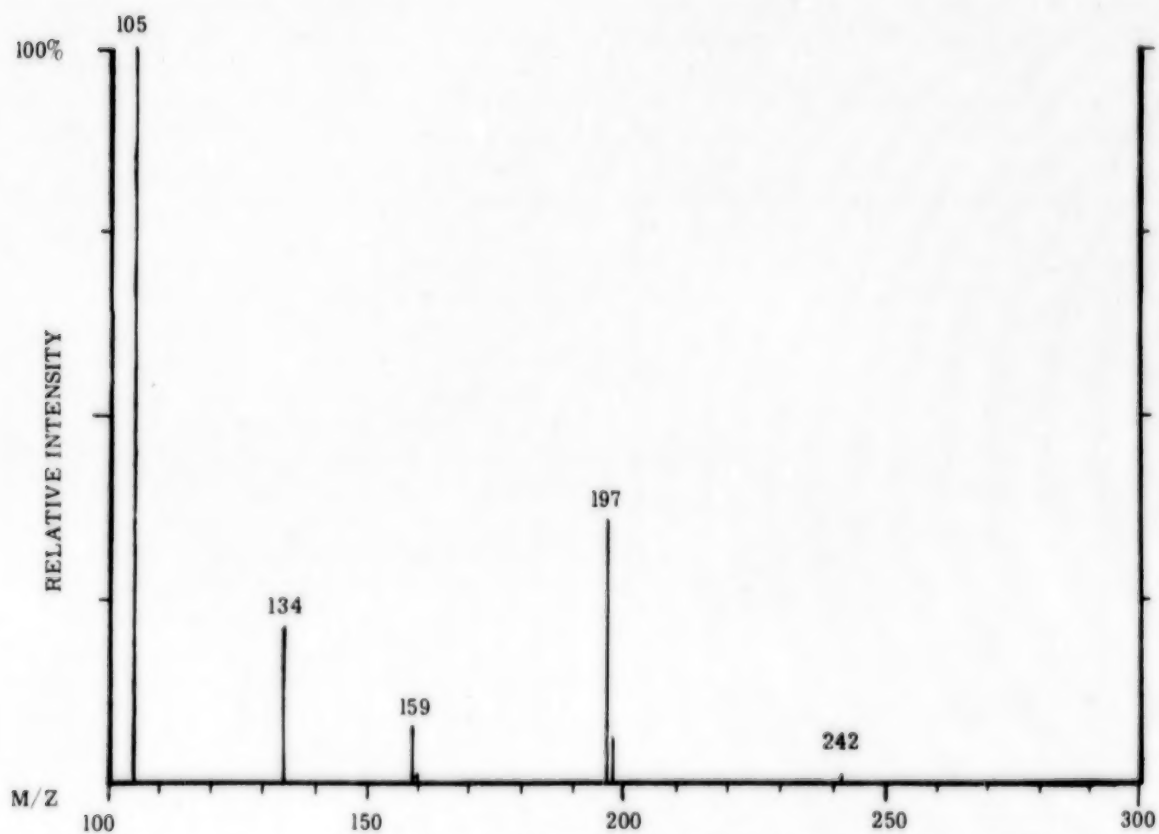


Figure 13. Methane chemical ionization mass spectra of first major component of headspace sample from bombing debris

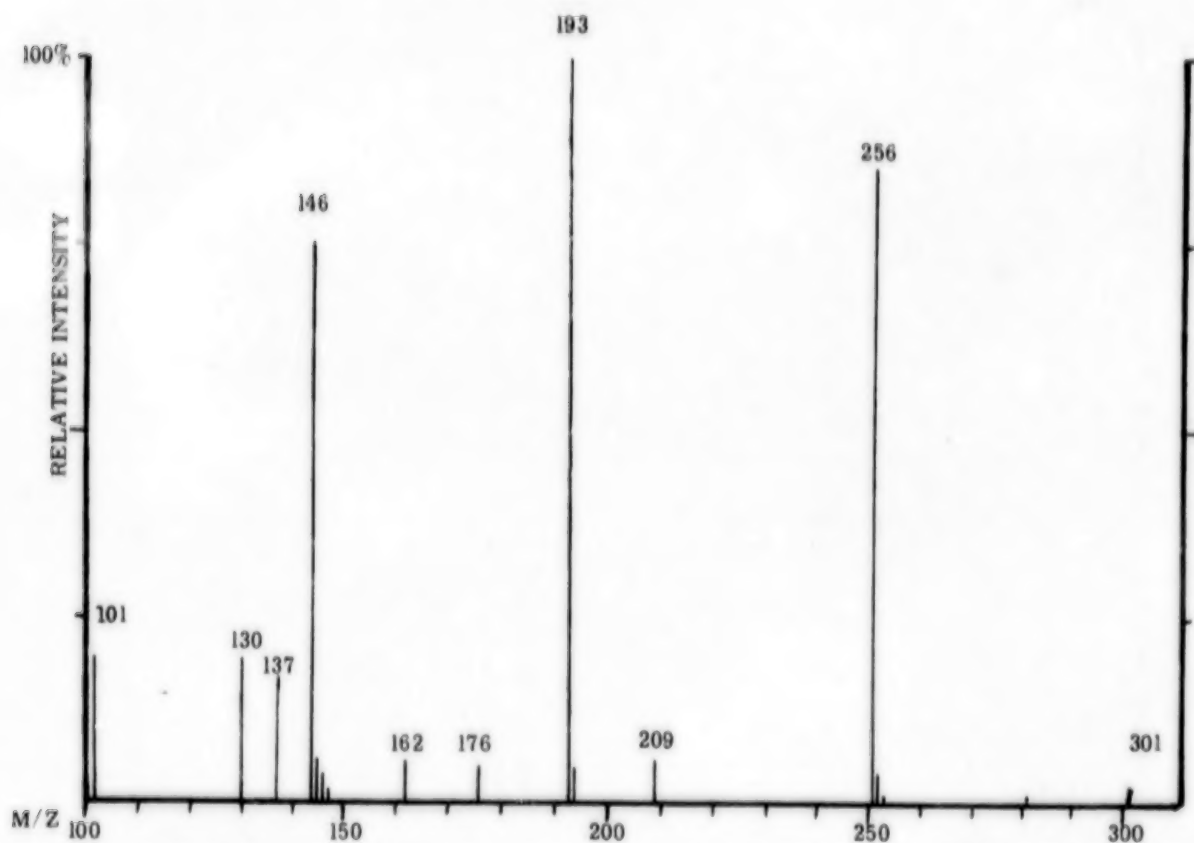


Figure 14. Methane chemical ionization mass spectra of second major component of headspace sample from bombing debris

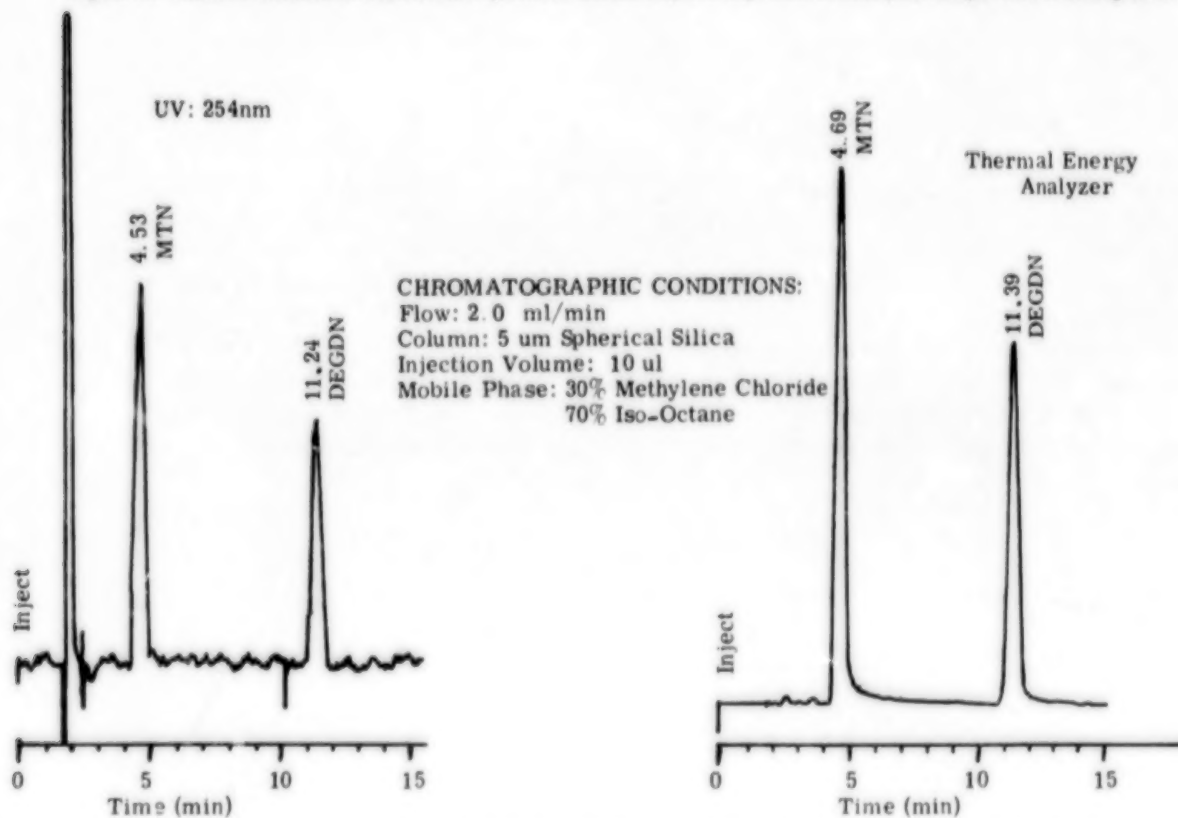


Figure 15. HPLC chromatogram of 83 ug metritol trinitrate (MTN) and 83 ug diethyleneglycol dinitrate (DEGDN)

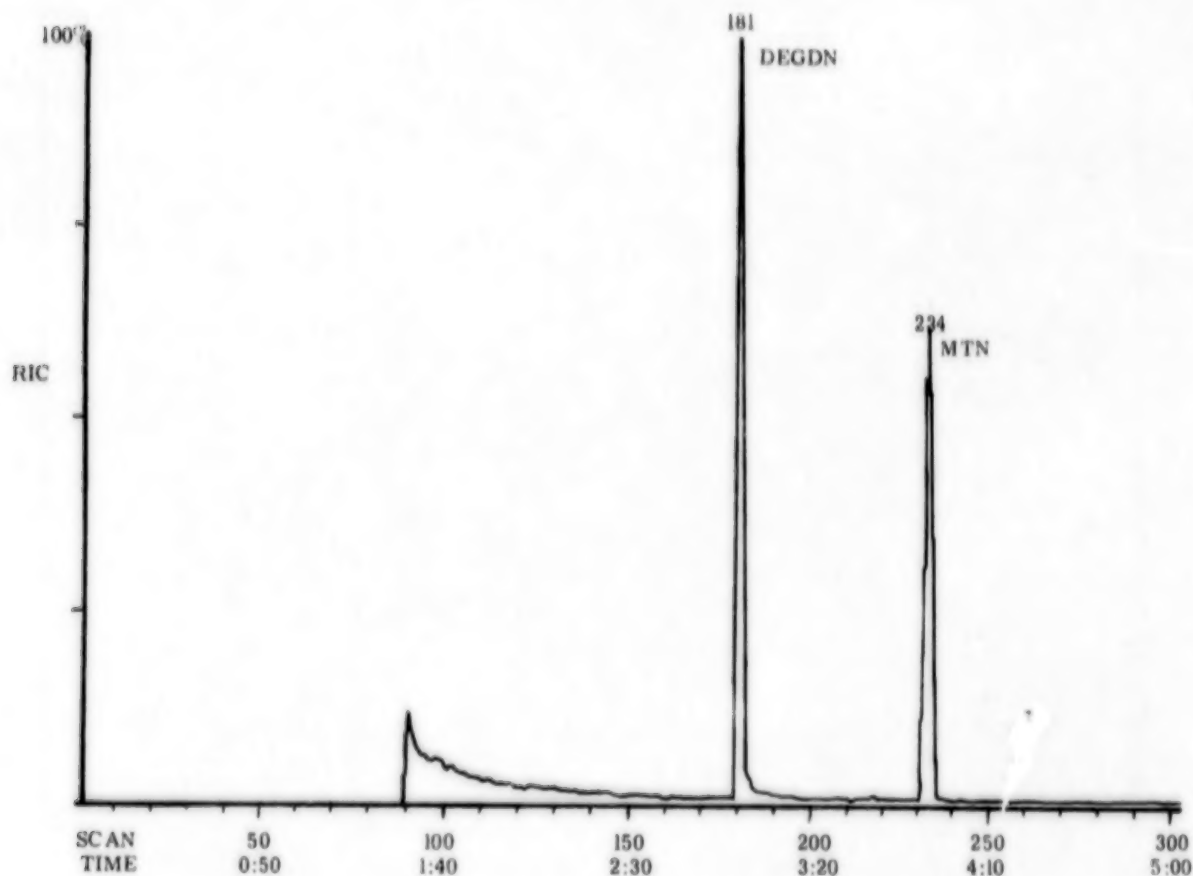


Figure 16. Total ion chromatogram of a 50/50 mixture of metriol trinitrate (MTN) and diethyleneglycol dinitrate (DEGDN)

cases were in standard references on explosives. The second explosive had been manufactured in this country for a number of years. However, none of the explosives were in the FBI's extensive collection and no spectral data was recorded for those explosives in any of the standard spectra reference libraries. There are hundreds of other explosives which are listed in common references for which the same statement could be made. There is

then a need to establish a comprehensive file of CI mass spectra of explosives, for with this data the compounds discussed above could have been identified with relatively little effort.

#### ACKNOWLEDGMENTS

We would like to thank Dr. Sphon and Dr. Mazola of the FDA for their high resolution mass spectroscopy and NMR work.



## DESCRIPTION OF A NITRO/NITROSO SPECIFIC DETECTOR FOR THE TRACE ANALYSIS OF EXPLOSIVES

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**ABSTRACT.** A nitro/nitroso specific detector for both capillary column gas chromatography (GC-TEA) and high-performance liquid chromatography (HPLC-TEA) is described. The sensitivity of GC-TEA at a signal-to-noise ratio of 3/1, is approximately 5 pg for ethylene glycol dinitrate (EGDN), glycerol trinitrate (NG), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5 trimethylene-2,4,6 trinitramine (RDX) and 25 pg for trinitro-2,4,6-phenylmethylnitramine (tetryl). The precision at the 1 ng level, expressed as relative standard deviations, was  $\pm 1.6\%$  for EGDN,  $\pm 1.4\%$  for NG,  $\pm 2\%$  for 2,4-DNT,  $\pm 1.3\%$  for TNT,  $\pm 5.7\%$  for RDX and  $\pm 2.6\%$  for tetryl. For HPLC-TEA, the precision at the 1 ng level for NG, isosorbide dinitrate (ISDN) and pentaerythritol tetranitrate (PETN) was  $\pm 2.3\%$ ,  $\pm 8.6\%$  and  $\pm 5.9\%$  relative standard deviations respectively. The linearity of the instrument response from 0.1–50 ng range has been demonstrated using NG, PETN, and ISDN, with correlation coefficients of 0.9942, 0.9963 and 0.9841, respectively. Confirmation of the identity of the compound under test is achieved by the use of parallel GC-TEA and HPLC-TEA analysis.

### INTRODUCTION

A variety of techniques have been used for the analysis of explosives. Some of the most commonly used techniques, such as thin layer chromatography (Douse, 1982; Kempe and Tannert, 1972; Peak, 1980; Twibell *et al.*, 1982; Yinon and Zitrin, 1981) polarography (Hetman, 1973; Whittack, 1975; Yinon and Zitrin, 1981), ultraviolet (Baaske *et al.*, 1983; Doali and Juhasz, 1974; Dalton *et al.*, 1975; Gelber and Papas, 1983; Krull and Camp, 1980; Yinon and Zitrin, 1981) and infrared spectroscopy (Meyers, 1977; Peimer *et al.*, 1980; Washington, 1976; Yinon and Zitrin, 1981) require large sample quantities and, in some cases, extensive clean-up procedures to minimize the interference problems and positively identify the un-

known explosives. The gas chromatography-electron capture technique (GC-ECD) provides a sensitive method for the analysis of explosives but suffers from detector overloading and contamination, and subsequent loss of sensitivity and linearity during the analysis of environmental samples unless great care is taken with respect to sample clean-up (Douse, 1981; Douse, 1982; Twibell *et al.*, 1982; Yinon and Zitrin, 1981). Chemical ionization mass-spectroscopy (CIMS), in conjunction with electron impact mass-spectroscopy (EIMS), has been used successfully for the positive identification of explosive compounds (Mach *et al.*, 1978; Yinon and Zitrin, 1977). Negative ion CIMS of explosives provides excellent sensitivity and selectivity for the detection of these compounds (Yinon

and Zitrin, 1981; Yinon, 1980). The on-line use of HPLC in conjunction with CIMS is a very selective method but lacks sensitivity because LC/MS interface only allows about 1% of the sample into the ion source (Parker *et al.*, 1982). Also, the high cost of the mass-spectroscopic techniques limits the widespread use of this approach.

In this report, we describe a nitro/nitroso specific detector, called the TEA analyzer, for the rapid, sensitive and selective determination of explosive residues. The TEA itself, and its detailed principle of operation, has been described previously (Fine *et al.*, 1975; Fine *et al.*, 1975; LaFleur and Mills, 1981; LaFleur and Morriseau, 1980). A brief description will be given in the "Experimental" section of this paper.

## EXPERIMENTAL

### Reagents

All solvents used were of distilled-in-glass grade (Burdick and Jackson). The explosives used in this study were glycerol trinitrate (NG), pentaerythritol tetranitrate (PETN), isosorbide dinitrate (ISDN), ethylene glycol dinitrate (EGDN), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), trinitro-2,4,6-phenylmethylnitramine (Tetryl).

### GC-TEA

A gas chromatograph (Hewlett Packard, Model 5840A), equipped with an on-column injector (SGE Scientific, Model OCI-3) was used. The fused-silica capillary column (DB-5) was 30 m long, 0.32 mm i.d. and had a 0.25  $\mu$ m film thickness. The carrier gas was helium at a head pressure of 18 psi. The injection port temperature was ambient. For the separation of the explosives shown in Figure 2, the oven temperature was held at 60°C for 1 minute, and then increased at 15°C/minute to 240°C, and then held at 240°C for 3 minutes. For the separation of the explosives shown in Figure 3, the oven temperature was programmed from 40°C to 260°C at a 10°C/min. rate.

The detector was a TEA analyzer (Thermo Electron, Model 610), operating in the nitro mode. The interface temperature was 285°C, and the pyrolyzer temperature was 900°C. The reaction chamber was held at 1.8 mm Hg, with an O<sub>3</sub> flow of 5 ml/minute. The cold trap was maintained at -100°C with a slush bath of ethanol and liquid nitrogen. The amount of material injected on column was 0.2  $\mu$ l - 1.0  $\mu$ l.

### HPLC-TEA

The high-performance liquid chromatographic system consisted of a solvent pump (Altex, Model 110) and an injector (Waters Associates, Model U6K). The column was a 10  $\mu$ m uBondapak CN, 30 cm long by 3.9 mm i.d. (Waters Associates). For screening EGDN, TNT, NG, PETN, and RDX, the solvent system was isooctane/methylene chloride/methanol in the ratio 165/35/10. The solvent flow rate was maintained at 1.5 ml/minute. Typically, the amount injected, on column, was 5-10  $\mu$ l. The TEA catalytic pyrolyzer was operated at 550°C. The reaction chamber vacuum was 1.8 mm Hg, with an O<sub>3</sub> flow rate of 5 ml/minute. The carrier gas was N<sub>2</sub>, at a flow rate of 20 ml/minute. The TEA cryogenic trap was maintained at -78°C with a slush bath of ethanol and solid carbon dioxide.

### DESCRIPTION OF THE TEA ANALYZER

The effluent from the chromatograph enters a catalytic pyrolyzer, where NO<sub>2</sub> is released from organic nitro compounds and simultaneously converted into NO by the catalytic surface. Solvent vapors and pyrolysis products are then removed by a cold trap which is maintained at about -100°C. The NO gas which survives the trap is reacted with ozone (O<sub>3</sub>) in the reaction chamber at reduced pressure to produce the characteristic infrared chemiluminescent reaction, the intensity of which is monitored by an infrared-sensitive photomultiplier tube (Figure 1). While the technique is sensitive at the picogram level, it is also highly selective. The rejection ration of the TEA to hydrocarbons and N-containing organics is greater than 10<sup>6</sup> to 1 (Fine *et al.*, 1975). A partial list of compounds which have been shown to give no response on the TEA is shown in Table 1. The selectivity stems from four factors. First, only compounds which have the NO<sub>2</sub> or NO functional groups can give a response. Second, the reactive species must survive the -100°C cold trap. For highly contaminated samples, a -160°C trap can be used. Third, the reactive species must react with O<sub>3</sub> to produce a chemiluminescent light in the narrow wavelength range of 0.6-2.8 microns. Fourth, the reaction with O<sub>3</sub> must be rapid enough to occur while the effluent is in the reaction chamber, and not in the vacuum pump.

## RESULTS AND DISCUSSION

Separation of the various explosives on GC and HPLC were developed. Figure 2 shows the injec-

# PRINCIPLE OF OPERATION

## Nitro Compounds

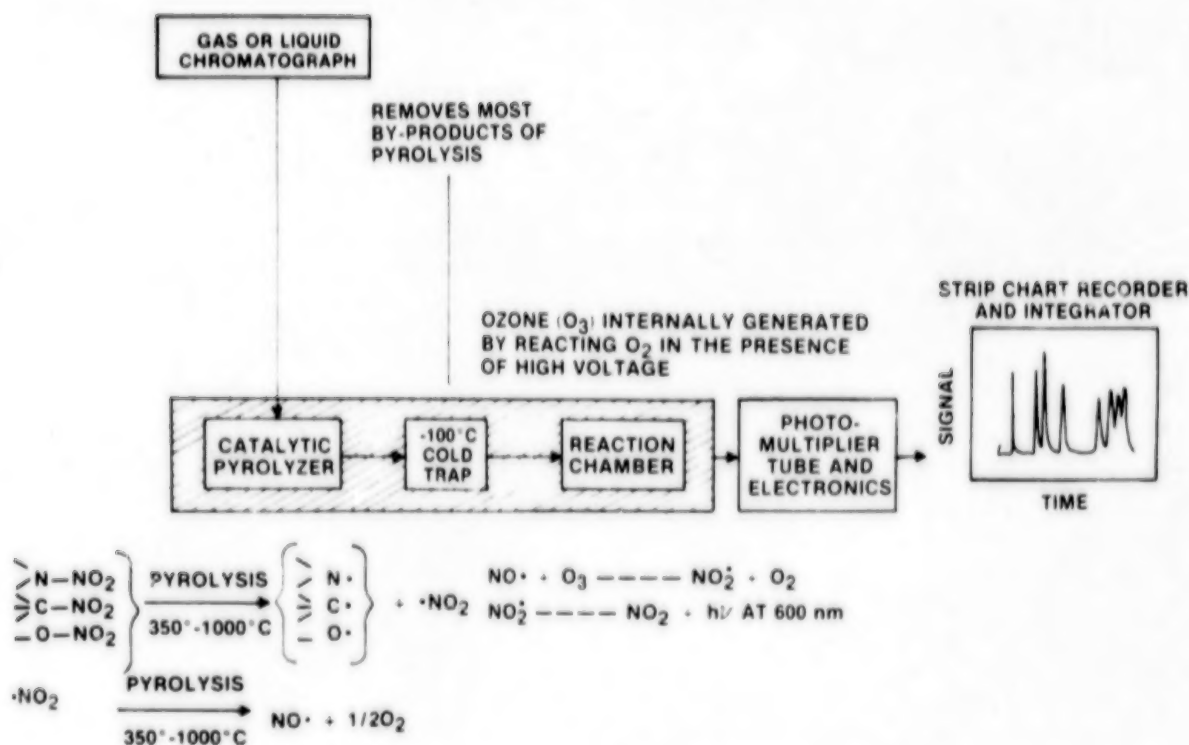


Figure 1. Principle of operation of the TEA Analyzer for nitro compounds.

tion of six common explosives—EGDN, NG, 2,4-DNT, TNT, RDX, and Tetryl at approximately 1 ng level on capillary GC-TEA. Under the GC conditions used, all six compounds were baseline resolved. For the separation of NG, 2,4-DNT, TNT, PETN and RDX, as shown in Figure 3, a slightly different chromatographic condition needs to be used to resolve PETN from TNT and RDX. Also, a reduced response for PETN on GC-TEA was observed due to the decomposition of the compound on the chromatographic system before it reaches the detector. This same phenomenon was also observed by Douse (1982) when an electron capture detector was used. Apparently, even under the ambient injection conditions, the lability of PETN limits the GC approach for detecting this compound.

Since liquid chromatography operates on a different set of parameters than gas chromatography, and it is amenable to thermally unstable compounds, the HPLC-TEA technique offers a complimentary approach to GC-TEA. LaFleur and Morriveau (1980) have already demonstrated the

detection of various explosives by HPLC-TEA using solvent programming techniques.

For the routine screening of a large number of samples for explosive residues, an isocratic condition might be more practical. Using a uBondpak CN column, we can separate EGDN, TNT, NG, PETN and RDX by HPLC-TEA, as shown in Figure 4. By increasing the polarity of the mobile phase, one can also screen for HMX. Thus, for thermally labile compounds such as PETN and HMX, HPLC-TEA can be used.

### Sensitivity.

The sensitivity attainable on the capillary column GC-TEA is demonstrated by the three chromatograms shown in Figure 5. Figure 5A is the chromatogram for 10 pg of NG, 8 pg of TNT and 7 pg of RDX, introduced on column. The three peaks are clearly discernible above the background. The minimum detectable level at a signal-to-noise ratio of 3/1, is estimated to be 4 pg for TNT and RDX, 5 pg for EGDN, NG and DNT and 25 pg for tetryl. Although the chromatograms

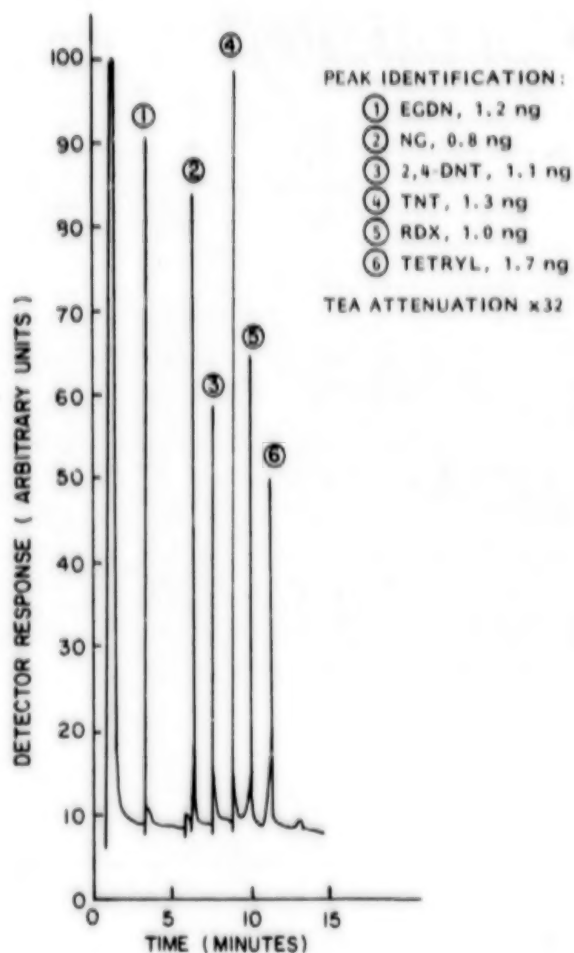


Figure 2. Analysis of six explosives on capillary column GC-TEA (Attenuation  $\times 32$ ). Peak identification is as follows. Peak 1-1.2 ng EGDN, Peak 2-0.8 ng NG, Peak 3-1.1 ng 2,4-DNT, Peak 4-1.3 ng TNT, Peak 5-1.0 ng RDX, Peak 6-1.7 ng Tetryl.

of Figure 5 were obtained with standard solutions, little degradation in performance is observed when analyzing complex explosive residue samples.

#### Precision.

For the HPLC-TEA, precision data has been demonstrated using NG, PETN and ISDN, at the 1 ng, 5 ng, 20 ng and 50 ng level injected on column (Yu and Goff, 1983), as shown in Table 2. At the 1 ng injection level, for example, the relative standard deviations were  $\pm 2.3\%$  for NG,  $\pm 5.9\%$  for PETN and  $\pm 8.6\%$  for ISDN. For capillary column GC-TEA, the precision, expressed as relative standard deviations, which was attained over 5 injections of approximately 1 ng on column, was  $\pm 1.6\%$  for EGDN,  $\pm 1.4\%$  for NG,  $\pm 2\%$  for 2,4-DNT,  $\pm 1.3\%$  for TNT,  $\pm 5.7\%$  for RDX and  $\pm 2.6\%$  for tetryl (Table 3).

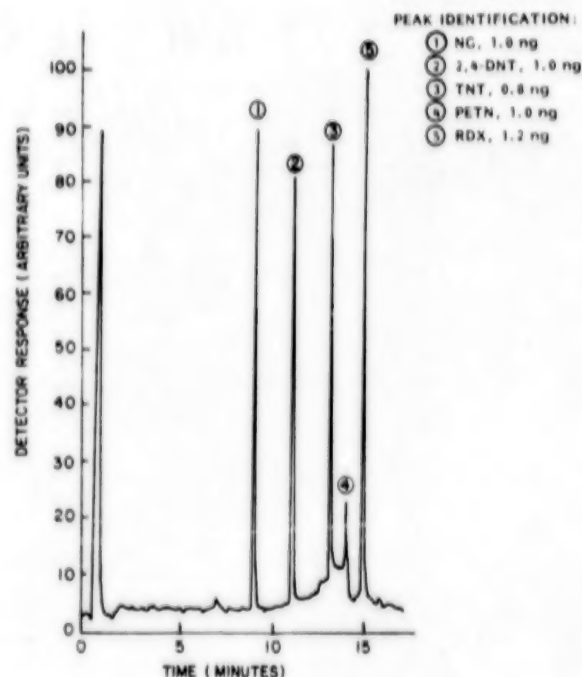


Figure 3. Analysis of five explosives on capillary column GC-TEA. Peak identification is as follows. Peak 1-1.0 ng NG, Peak 2-1.0 ng 2,4-DNT, Peak 3-0.8 ng TNT, Peak 4-1.0 ng PETN, Peak 5-1.2 ng RDX.

#### Linearity.

The detector has been shown to be linear over 6 orders of magnitude (Fine et al, 1975). LaFleur and Morriveau (1980) also demonstrated the linearity of the detector response as a function of concentration for RDX and PETN (Figure 6). The points were obtained by ten determinations at each of the three concentration levels. For RDX, the concentration levels were 219, 2190 and 21900 ng/mL. For PETN, the concentration levels were 320, 3120 and 31200 ng/mL. The linearity of response as indicated by the correlation coefficients was greater than 0.999. The linearity of the detector has also been demonstrated as a function of the number of nitrosyl-containing functional groups per molecule for nitrate esters and nitramines (Figure 7). For the nitrate esters (compounds with  $-\text{ONO}_2$  functional groups), the compounds used were isosorbide-5-mononitrate (5-ISMN), ISDN, (two  $-\text{ONO}_2$ ) NG (three  $-\text{ONO}_2$ ) PETN (four  $-\text{ONO}_2$ ). For nitramines, 1-nitroguanidine; RDX (a trinitramine) and HMX (a tetranitramine) were used. For each compound ten determinations were performed. The linearity of both plots, expressed as correlation coefficients, was greater than 0.99.



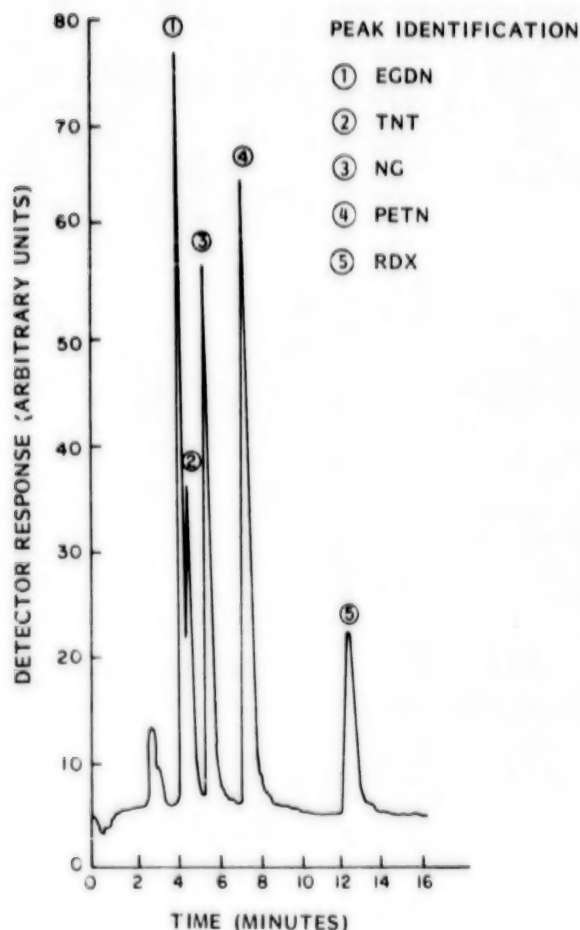


Figure 4. Analysis of five explosives by HPLC-TEA (Attenuation  $\times 16$ ). Peak identification is as follows. Peak 1-8.0 ng EGDN, Peak 2-64 ng TNT, Peak 3-8.0 ng NG, Peak 4-8.0 ng PETN, Peak 5-8.0 ng RDX.

In this paper we establish the linearity for NG, ISDN and PETN from 0.1-50 ng with the corresponding linear regression correlation coefficients of 0.9942, 0.9841 and 0.9963, respectively (Figure 8). Quadruple determinations were made for each point.

#### Parallel GC-TEA/HPLC-TEA Confirmation.

The operation of a selective detector with both GC and HPLC offers a novel self-confirmatory capability. In GC, separation of the compounds is achieved by differences in vapor pressure and solubility in the liquid phase of the column. In HPLC, however, polarity, physical size, and shape characteristics determine the chromatographic selectivity. The result is that the elution order of the explosives is different on GC and on HPLC. Thus, an analysis which is highly specific could be interpreted as confirmatory by an examiner if three criteria are met:

- (i) The peak elutes at the proper retention time on both GC-TEA and HPLC-TEA.
- (ii) Both chromatograms are relatively clean.
- (iii) Identical quantitation is achieved on both systems.

If some doubt exists because of multiple peaks, the compound can be isolated off HPLC-TEA by collecting the effluent at the retention time indicated by a previous HPLC-TEA run before the compound enters the pyrolyzer, concentrated and reinjected on both HPLC-TEA and GC-TEA. A single peak of the proper quantitation eluting at the proper retention time, can be taken as confirmatory. Data, based on this principle, are presented in the following paper (Fine, *et al.*, 1983). Parallel GC-TEA/HPLC-TEA determinations have been used successfully in the N-nitrosamine field, when the amount of sample was too small to be handled by other methods (Fine 1980, Fine *et al.*, 1977) and have been interpreted by workers in that field as confirmatory.

#### CONCLUSION

The sensitivity of the TEA analyzer for explosive analysis in the low picogram (pg) range has been demonstrated. This sensitivity level is maintained even when analyzing complex samples because of the unique selectivity of the detector. The advantages of using a selective detector are several. Aside from the benefits of excellent sensitivity, the need for extensive sample clean-up procedures prior to sample analysis is eliminated, with subsequent savings in the time spent for sample preparations and material costs.

The parallel use of HPLC-TEA and GC-TEA techniques increases the selectivity of the detector and serves as a confirmatory approach.

The linearity of detector response in the low pg and nanogram (ng) range renders the TEA technique suitable for the sub part per billion (ppb) level determinations of explosives in post-blast debris, handswabs, wastewater effluents, air samples, and human plasma. The practical application of this technique will be presented in the following papers.

#### ACKNOWLEDGEMENTS

We thank D. Reutter of the FBI for many valuable discussions. The technical assistance of J. Buckley is gratefully acknowledged.

Peak	Amount A.	Injected B.	Picograms C.
① NG	10	20	50
② TNT	8	16	40
③ RDX	7	14	35

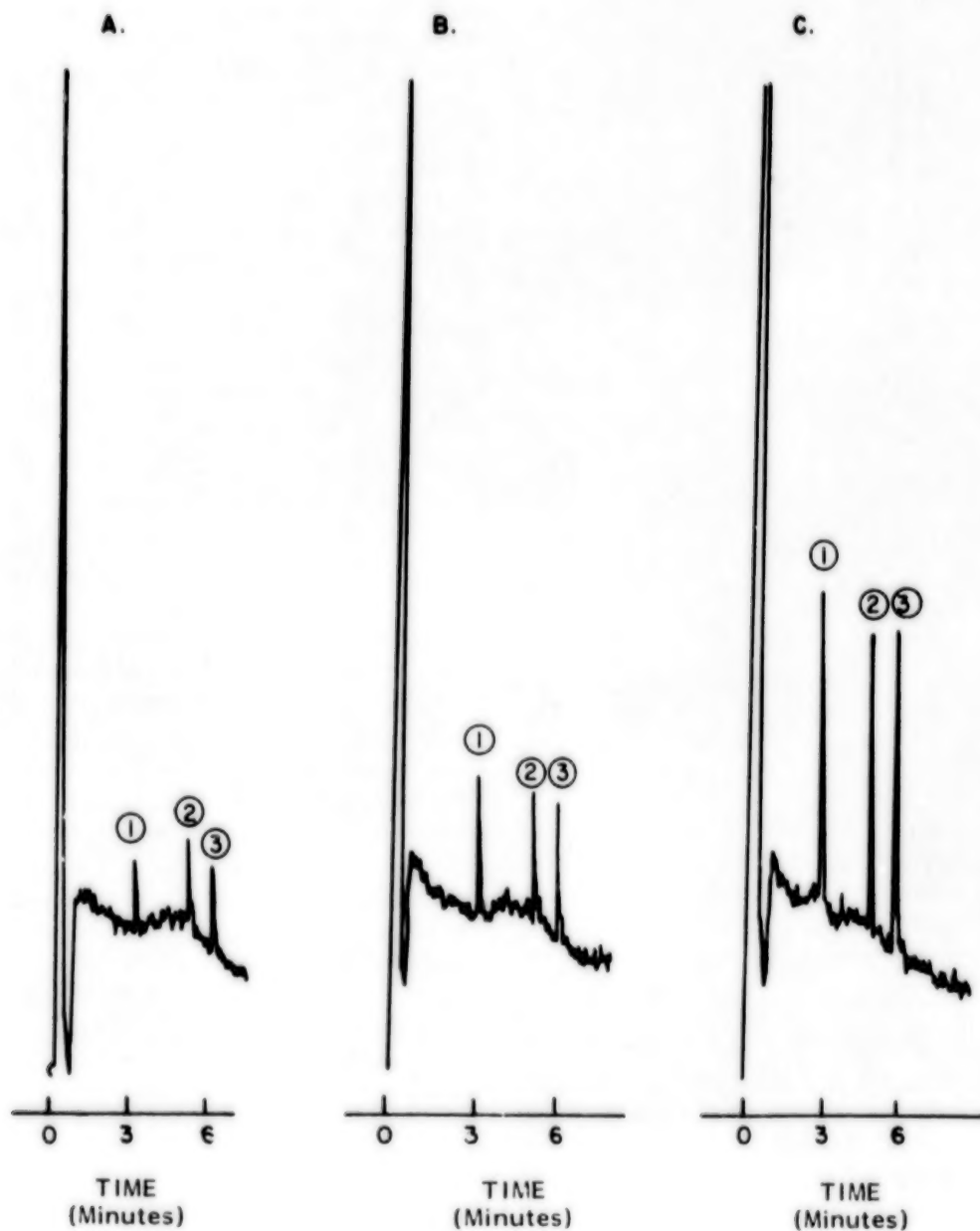


Figure 5. Sensitivity of capillary column GC-TEA, for 0.2 ul injection of NG (Peak 1), TNT (Peak 2), and RDX (Peak 3).



## DETECTOR RESPONSE AS A FUNCTION OF CONCENTRATION FOR PETN AND RDX

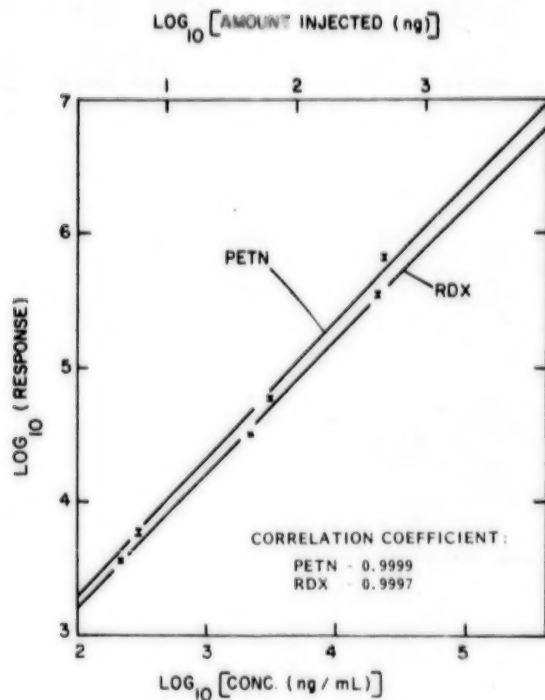


Figure 6. TEA Analyzer linearity response for PETN and RDX. PETN concentration levels were 219, 2190 and 21900 ng/ml. RDX concentration levels were 320, 3120, and 31200 ng/ml.

## DETECTOR RESPONSE VS THE NUMBER OF NITROSYL-CONTAINING FUNCTIONAL GROUPS PER MOLECULE

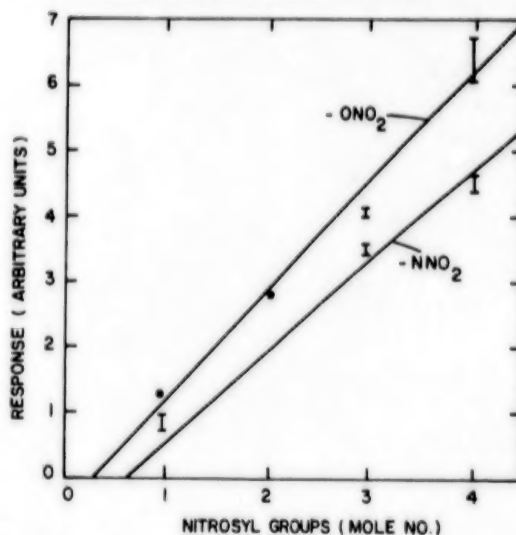


Figure 7. TEA Analyzer linearity response, demonstrated as a function of the number of nitrosyl-containing functional groups per molecule. Nitrate esters (with  $-\text{ONO}_2$  group) and nitramines (with  $\text{NNO}_2$  groups) were employed.

TABLE 1. REPRESENTATIVE LIST OF COMPOUNDS WHICH WERE FOUND TO GIVE NO INTERFERENCE ON THE TEA

Acetic acid	Ethyl acetate	Oxalic acid
Acetone	Ethyl carbamate	n-Pentane
Acetonitrile	Ethylene glycol	Phenyl hydrazine
Alizarin red	Fluorobenzene	d,l-Phenylalanine
Ammonia (gas)	Gasoline	p-Phenylazoaniline
Benzene	Glycerol	Phosphoric acid
Benzylsalicylate	d-Glucose	Propane (gas)
2-Butoxy ethanol	Glutamic acid	Pyridine
Carbon dioxide	n-Hexane	Quinine
Carbon disulfide	Hydrogen (gas)	Sodium acetazolamide
Carbon monoxide (gas)	Hydroquinone	Sulfadiazine
Carbon tetrachloride	8-Hydroxyquinoline	Sulfanilic acid
Chloral hydrate	Inosine	Tetrahydrofuran
Chlorobenzene	d,l-iso-leucine	Theophylline
1-Chloropropane	Methane (gas)	Toluene
2-Chloropropane	Methyl acetate	2,4,6-Trichlorophenol
Cyclohexane	N-Methyl bisacrylamide	2,2,4-Trimethylpentane
Cyclopentane	2-Methyl butane	d,l-Tryptophane
1,2-Dichloroethane	Methyl formamide	Urea
2,3-Dichloropropane	Methyl isobutyl ketone	Uric acid
Diethylether	Methyl orange	Urethane
Dimethylamine (gas)	Methyl red	Water
p-Dioxane	Napthalene	Xylene
Diphenylamine	Nitrogen (gas)	

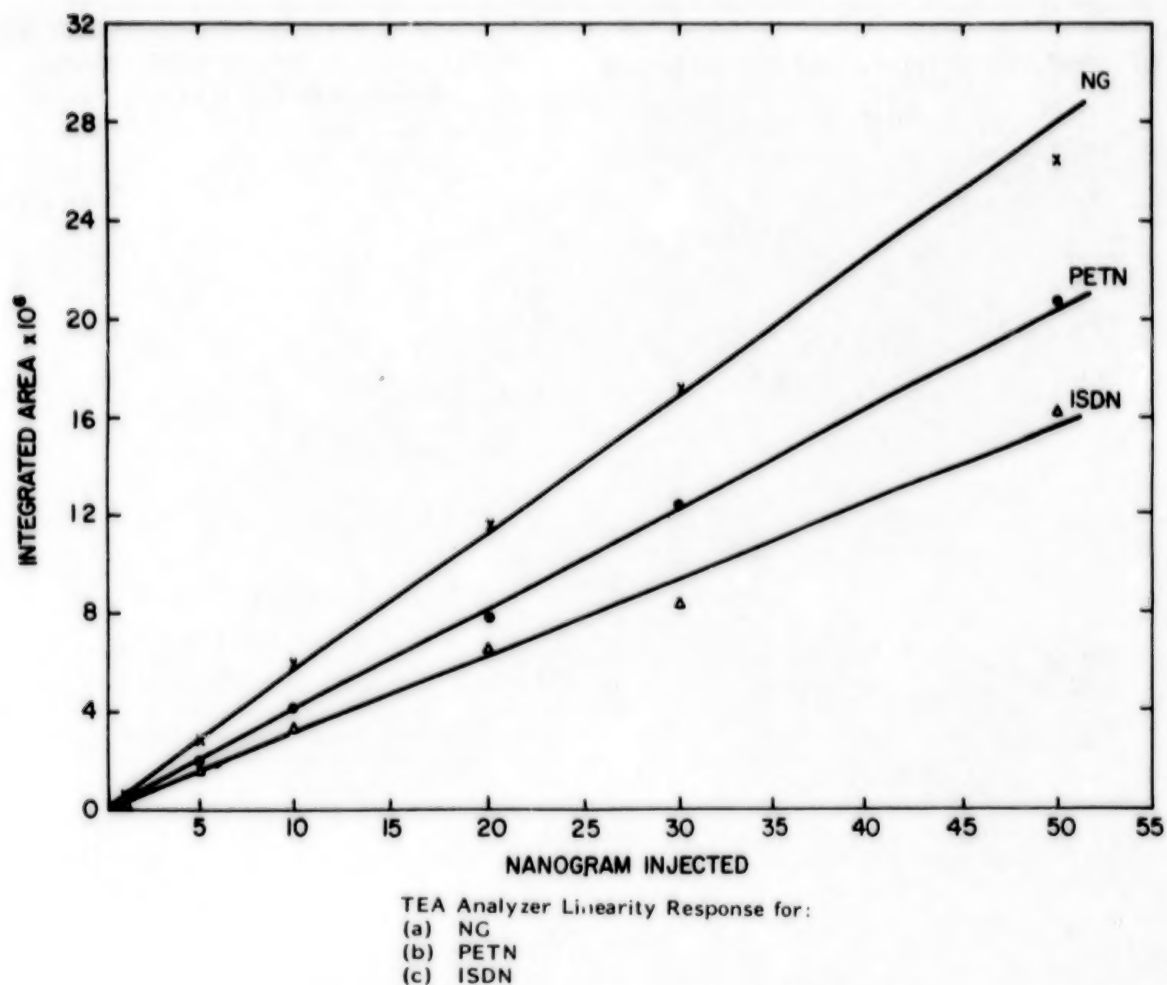


Figure 8. TEA Analyzer linearity response for NG, PETN, ISDN at 0.1-50 ng range.

TABLE 2. PRECISION OF HPLC-TEA

Compound	Amount Injected ng	Response (X) <sup>a</sup>	(S) <sup>b</sup>	(Sr) <sup>c</sup>
NG	1.0	$5.28 \times 10^5$	0.12	2.3
	5.0	$2.77 \times 10^6$	0.11	4.1
	20.0	$1.16 \times 10^7$	0.04	3.5
	50.0	$2.65 \times 10^7$	0.09	3.4
ISDN	1.0	$1.41 \times 10^5$	0.12	8.6
	5.0	$8.25 \times 10^5$	0.61	7.3
	20.0	$3.25 \times 10^6$	0.21	6.5
	50.0	$1.62 \times 10^7$	0.12	7.4
PETN	1.0	$4.41 \times 10^5$	0.25	5.9
	5.0	$2.04 \times 10^6$	0.04	2.2
	20.0	$7.85 \times 10^6$	0.34	4.3
	50.0	$2.08 \times 10^7$	0.05	2.4

<sup>a</sup>(X) = MEAN VALUE FOR 5 DETERMINATIONS, ARBITRARY UNITS.

<sup>b</sup>(S) = STANDARD DEVIATION.

<sup>c</sup>(Sr) = RELATIVE STANDARD DEVIATION EXPRESSED AS A PERCENT.

TABLE 3. PRECISION OF CAPILLARY GC-TEA ON EXPLOSIVES AT THE NANOGRAM LEVEL  
(n = 5)

Compound	Amount Injected ng	Integrated Area	Std. Dev.	% Rsd
EGDN	1.2	$1.80 \times 10^4$	0.03	1.6
NG	0.8	$1.51 \times 10^4$	0.02	1.4
2,4-DNT	1.1	$1.14 \times 10^4$	0.02	2.0
TNT	1.3	$1.88 \times 10^4$	0.02	1.3
RDX	1.0	$1.31 \times 10^4$	0.07	5.7
TETRYL	1.7	$1.07 \times 10^4$	0.03	2.6

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## APPLICATIONS OF THE NITRO/NITROSO SPECIFIC DETECTOR TO EXPLOSIVE RESIDUE ANALYSIS

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**ABSTRACT.** The specificity of the TEA<sup>®</sup> Analyzer interfaced to a gas chromatograph (GC-TEA) and/or a liquid chromatograph (HPLC-TEA) renders the technique a useful tool for the analyses of explosive residues in a wide variety of forensic and environmental applications. Specific applications to the analyses of explosive residues are described, including post-explosion debris and washings from persons who have handled explosives. Examples of environmental data are also included.

### INTRODUCTION

The ideal technique for the ultra-trace analysis of explosives would be both simple and rapid, require minimal sample clean-up, be sensitive to as little as 1-10 pg (picograms,  $10^{-12}$ g) quantities of all the compounds of interest, and would work equally well on both complex samples from the real world and on high-grade laboratory standards made up in pure solvents. The TEA Analyzer has been designed to respond only to nitro- and nitroso-containing compounds. Its principle of operation was presented in detail in the previous paper by Goff *et al.* (1983). The practical application of the detector in the forensic science area will be discussed here.

The possible application of the TEA analyzer to the problem of the analysis of organic nitro compounds has been addressed recently by LaFleur and Mills (1981) Maddock *et al.* (1983), Phillips *et al.* (1983) and Yu and Goff (1983, a,b). The performance of the TEA analyzer as a detector for explosives in high-performance liquid chromatography and gas chromatography has been described by LaFleur and Morriveau (1980), and LaFleur and Mills (1981), respectively. Three laboratories have developed procedures for the routine analysis of nitrate esters such as NG,

ISDN and PETN in blood at levels as low as 100 pg/ml. A comparison of the TEA analyzer with three other GC detectors; electrolytic conductivity, thermionic and electron capture, has been made by Phillips *et al.* (1983) for the analysis of nitroaromatics such as nitrobenzene, and the dinitrotoluenes in sludge wastes. Douse (1983) recently demonstrated the low picogram detection of explosives using silica capillary column gas chromatography with a TEA analyzer. This paper expands the applicability of the TEA analyzer for trace explosive residue analysis, to the low picogram level, on real world samples such as pieces of explosives, post-blast residues and handswabs. It is also shown that by using parallel HPLC-TEA and GC-TEA techniques it is possible to confirm the identity of the compound if the confirmatory criteria described in the preceding paper are met.

### EXPERIMENTAL PROCEDURES

#### Reagents

All solvents were of a grade which had been distilled in glass (Burdick and Jackson). The explosives used in this study were glycerol trinitrate (NG), pentaerythritol tetranitrate (PETN), ethylene glycol dinitrate (EGDN), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), cyclo-1,



3,5-trimethylene-2,4,6-trinitramine (RDX), trinitro-2,4,6-phenylmethyl-nitramine (Tetryl), and cyclotetramethylene tetranitramine (HMX).

## **SAMPLE PREPARATION**

### **a. Explosives.**

Small pieces of military and commercial explosives were dissolved in acetone to a concentration of 1%. The samples were then diluted in methanol to obtain a 10 ppm (weight/volume) solution. No clean-up was used.

### **B. Post-blast debris.**

Post-blast debris was collected from three test bombs (TNT, C4, and detonating cord), which were detonated by the FBI at the U.S. Marine demolition range at Quantico during January 1983. The bombs were made by placing the explosive inside a 40-gallon metal trash can, with a stone weight on the lid. Blasting caps, equipped with a safety fuse, were used to detonate the devices. For TNT, a 1 lb. demolition block was used; for C4, a 1 1/4 lb. charge; and for the detonating cord alone, about 15 feet was wrapped around the can. After detonation, about 500 g of debris including metal fragments, soil and fabric were collected and sent to Thermo Electron for analysis.

About 50 g of assorted debris was placed in a beaker (the metal fragments had to be cut so that they would fit into the beaker). After sonication in methylene chloride for 10 minutes, the methylene chloride was concentrated to 15 ml on a rotary evaporator, filtered through a Millex-SR filter and then concentrated under a stream of N<sub>2</sub> gas to 2 ml. Aliquots were then analyzed by both GC-TEA and HPLC-TEA.

### **C. Post-blast air sample.**

A Thermo sorb/N (Thermo Electron) N-nitrosamine air sampling cartridge developed by Rounbehler et al (1980) was evaluated for its capability of trapping post-blast air samples. Following the detonation of a dynamite bomb at the FBI Quantico demolition range in April, 1982, 10 liters of air was drawn through a cartridge with a bicycle pump. The cartridge was capped and sent to Thermo Electron for analysis.

The Thermo sorb/N cartridge was analyzed in the conventional manner by eluting with 1.8 ml of methylene chloride/methanol (75/25) into a sample vial. The solution was then analyzed by HPLC-UV-TEA on a uBondapak CN column, using a solvent system of isooctane/methylene

chloride/methanol (75/20/5) at a flow rate of 1.5 ml/minute.

### **D. Handswab experiments.**

The following were used for the test: C-4, gel dynamite, a plastic explosive and a piece of a letter bomb. Four volunteers held a small piece of explosive (approximately 1 x 3 cm) in the hand for 1 minute. After 15 minutes, the palm area was washed twice with a cotton swab soaked in acetone, a proven technique used by Douse (1982), Twibell et al (1982 a,b). The swabs were squeezed to dryness, and the acetone washings were then analyzed directly. Aliquots were then analyzed by GC-TEA and HPLC-TEA.

### **GC-TEA**

A gas chromatograph (Hewlett Packard, Model 5840A), equipped with an on-column injector (SGE Scientific, Model OCI-3) was used. The fused silica capillary column (DB-5) was 30 m long, 0.32 mm i.d. and had a 0.25  $\mu$ m film thickness. The carrier gas was helium at a head pressure of 18 psi. The injection port temperature was ambient. The oven temperature was held at 60°C for 1 minute, and then increased 15°C/minute to 240°C, and then held at 240°C for 3 minutes. The detector was a TEA analyzer (Thermo Electron, Model 610), operating in the nitro mode. The interface temperature was 285°C, and the pyrolyzer temperature was 900°C. The reaction chamber was held at 1.8 mm Hg, with an O<sub>2</sub> flow of 5 ml/minute. The cold trap was maintained at -100°C with a slush bath of ethanol and liquid nitrogen. The amount of material injected on column was 0.2  $\mu$ l - 1.0  $\mu$ l.

### **HPLC-TEA**

The high-performance liquid chromatographic system consisted of a solvent pump (Altex, Model 110) with an injector (Waters Associates, Model U6K). The column was a 10  $\mu$ m uBondapak CN, 30 cm long by 3.9 mm i.d. (Waters Associates). For most of the work, two detectors, connected in series, were used. The column effluent flowed first through a variable wavelength UV detector, set at 254 nm (Schoeffel, Model 770) and then into a TEA analyzer (Thermo Electron, Model 510). Some of the data were collected with only the TEA analyzer. For screening 2,4-DNT, EGDN, TNT, NG, PETN, tetryl and RDX, the solvent system was isooctane/methylene chloride/methanol in the ratio 165/35/10. For screening NG, PETN, RDX and HMX, the ratio of solvents was



60/30/10. The solvent flow rate was maintained at 1.5 ml/minute. Typically, the amount injected, on column, was 25  $\mu$ l. The TEA catalytic pyrolyzer was operated at 550°C. The reaction chamber vacuum was 1.8 mm Hg, with an O<sub>2</sub> flow rate of 5 ml/minute. The TEA carrier gas was N<sub>2</sub>, at a flow rate of 20 ml/minute. The TEA cryogenic trap was maintained at -78°C with a slush bath of ethanol and solid carbon dioxide.

## RESULTS AND DISCUSSION

### Explosives

Parallel GC-TEA and HPLC-TEA chromatograms are shown in Figure 1 for a sample of gelatin dynamite, and in Figure 2 for double-based smokeless rifle powder. The dynamite sample gave only two peaks, one due to NG and the other to EGDN. The double-based smokeless powder sample gave only a single peak, due to NG. Constituents other than the explosive components (such as plasticizer) did not interfere with either

the GC-TEA or HPLC-TEA analyses.

Figure 3 is the HPLC-UV-TEA chromatograms for C-4, Flex-X and a sample cut from a defused letter bomb of Middle East origin. For C-4, RDX is the major peak, with a small amount of HMX also being present. Flex-X, was shown to contain only PETN. PETN was also the only explosive found to be present in the letter bomb.

Although all five samples undoubtedly contained a multitude of materials other than the explosive constituents (plasticizers, etc.), no extraneous peaks were observed, even though no clean-up was used prior to analysis. It should be noted that although the UV detector is capable of far greater sensitivity at lower wavelengths, this high sensitivity is achievable only for standards. In all the data reported here, which include plasticizers etc., the greater sensitivity of the lower wavelengths is more than offset by the poor selectivity. Thus on an extract of a 'real' explosive, the peak due to the explosive would be drowned by the peak due to the impurities.

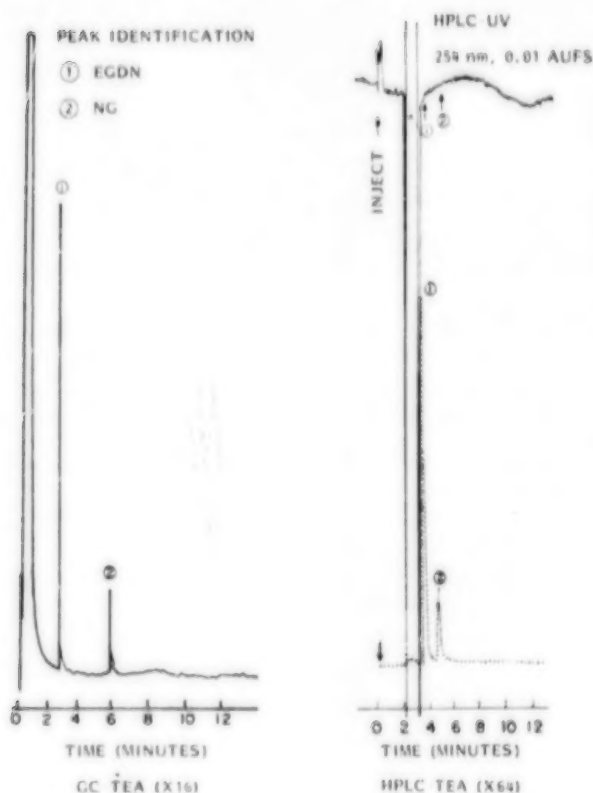


Figure 1. Chromatograms on GC-TEA, and HPLC-UV-TEA of a 10 ppm extract from gelatin dynamite. GC-TEA was obtained with 1  $\mu$ l injection, with peak 1 being 0.65 ng of EGDN and peak 2 due to 0.25 ng of NG. For HPLC, 20  $\mu$ l was injected on column. The EGDN peak was 13 ng, and the NG peak was 4.9 ng.

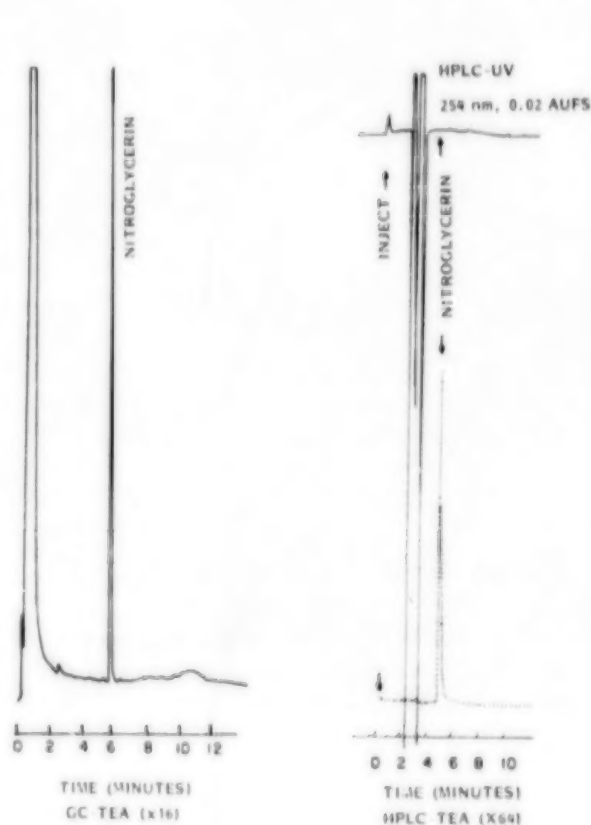


Figure 2. Chromatograms of GC-TEA and HPLC-UV-TEA of 10 ppm extract of double-based smokeless rifle powder. For GC-TEA, a 0.5  $\mu$ l injection was used, with the NG peak due to 1.1 ng of NG. For HPLC-TEA, 7  $\mu$ l was injected, with the NG peak being 15 ng.

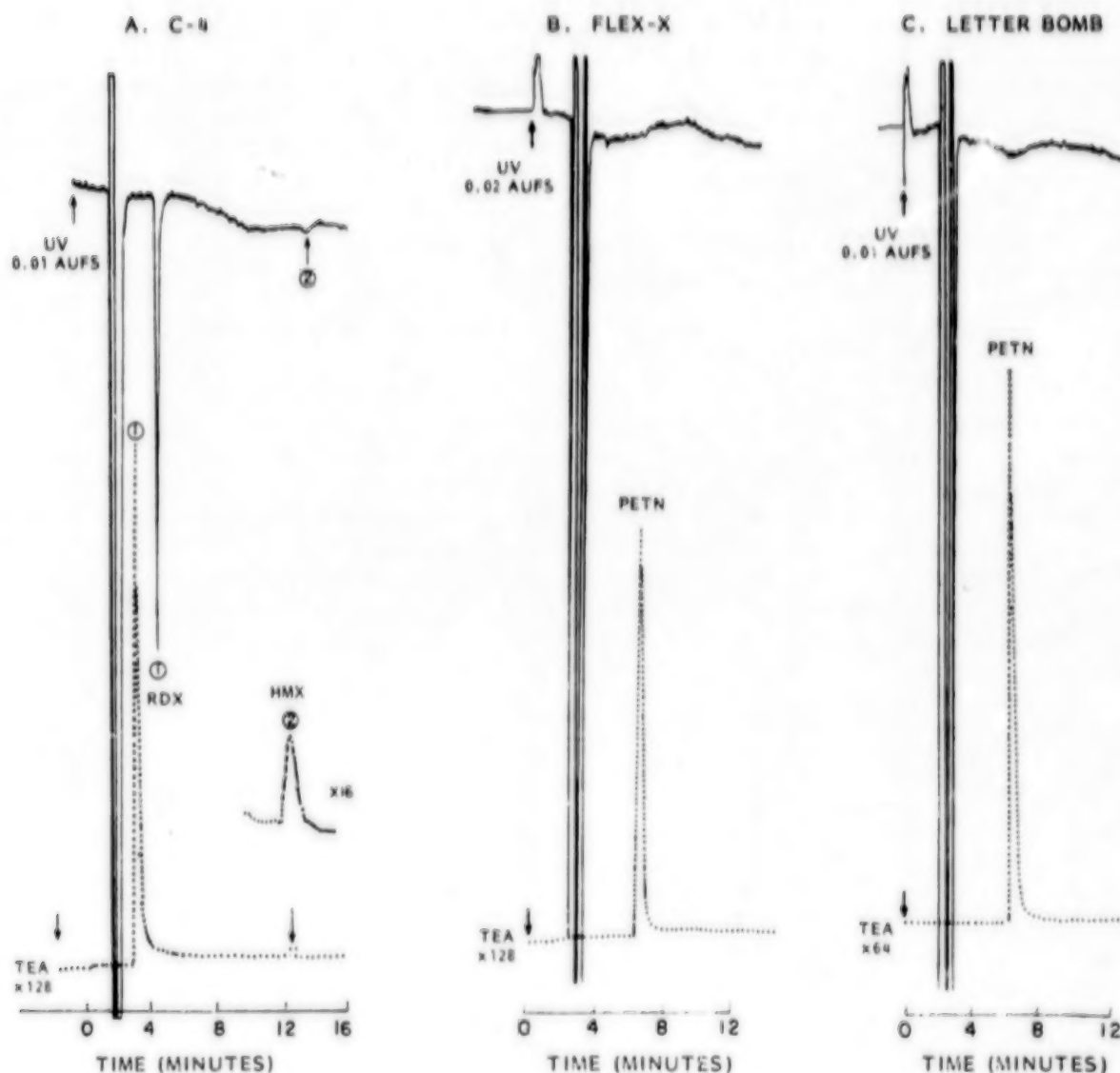


Figure 3A. Chromatogram on HPLC-UV-TEA for 10  $\mu$ l injection of a 10 ppm extract of C-4. Peak 1, at the retention time of RDX, was 117 ng. Peak 2, due to HMX, corresponds to 4.2 ng. 3B. Chromatogram on HPLC-UV-TEA for 3  $\mu$ l injection of a 10 ppm extract of Flex-X. The single peak was due to 38 ng of PETN. 3C. Chromatograms on HPLC-UV-TEA for 5  $\mu$ l injection of a 10 ppm extract of a letter bomb. The single peak was due to 33 ng of PETN.

#### Post-blast Debris

From the chromatogram of the extract of the TNT bomb (Figure 4), the TNT component of the total explosive residue was determined to be only 0.3%. On GC-TEA, the amount present in a 1  $\mu$ l injection of the debris extract was 0.1 ng EGDN, 4.4 ng NG, 0.15 ng 2,4-DNT, 0.03 ng TNT and 0.5 ng RDX.

For the detonating cord debris, (Figure 5), the GC-TEA showed a trace of EGDN, and a considerable amount of NG. The HPLC-TEA showed NG, as well as a trace of PETN (PETN partially decomposed in the GC). For debris from the C-4

bomb (Figure 6), 9 ng of RDX, 7.8 ng of PETN and 5 ng of NG were found in a 20  $\mu$ l injection on HPLC-TEA. Presumably, the cross contamination of all three samples was from the Quantico demolition range itself, which had been in continuous use for over 40 years.

The data in Figures 4-6 demonstrate the capability of the TEA analyzer in identifying post-blast explosive debris at the picogram level, even when the only sample preparation was extraction of the organic residue into a suitable solvent. Again, clean-up was unnecessary since there were few interfering peaks.

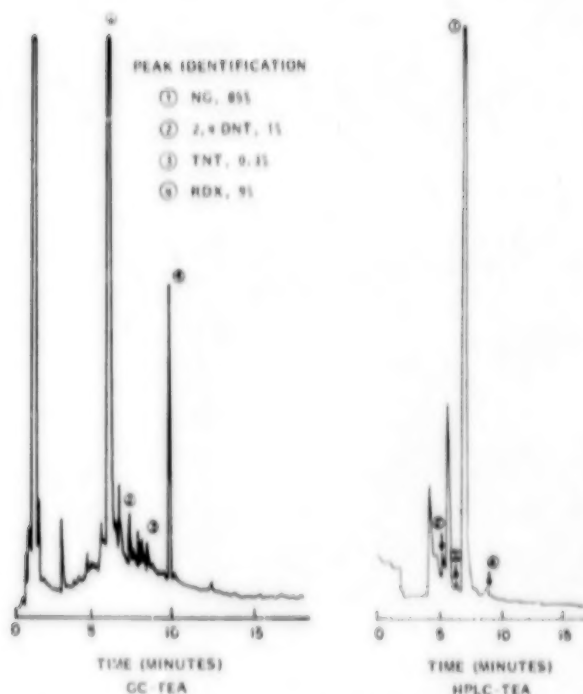


Figure 4. Chromatograms on GC-TEA and HPLC-TEA of extracts from post blast debris following an explosion of a TNT bomb. On GC-TEA ( $\times 16$ ), a 0.5  $\mu$ l injection of debris extract gave 4.4 ng of NG, 0.15 ng of 2,4-DNT, 0.03 ng of TNT and 0.5 ng of RDX. For HPLC-TEA ( $\times 32$ ) a 20  $\mu$ l injection was used.

#### Post-blast Air Sample

The TEA chromatogram, shown in Figure 7, shows the presence of EGDN, which is characteristic of a dynamite blast. The minimum detectable level of EGDN is less than the 9 ng shown in Figure 7. The minimum detectable level could be further enhanced by taking a larger air sample.

Similar experiments with an RDX and a TNT bomb were unsuccessful. Further work is needed to determine whether the cartridge would have trapped and released these compounds if they had been present in the post-blast air.

#### Handswab Experiments

Figure 8 shows the chromatograms for the gel dynamite handswab. Both EGDN and NG are seen to be present in relatively large quantities (the TEA analyzer was on attenuation  $\times 128$  for GC and  $\times 256$  for HPLC). For the handswab from C-4, only a single chromatographic peak due to RDX was observed (Figure 9). For plastic explosive, see Figure 10, the handswab extract contained mainly PETN, with only a trace of NG. The GC-TEA chromatogram shows the typical

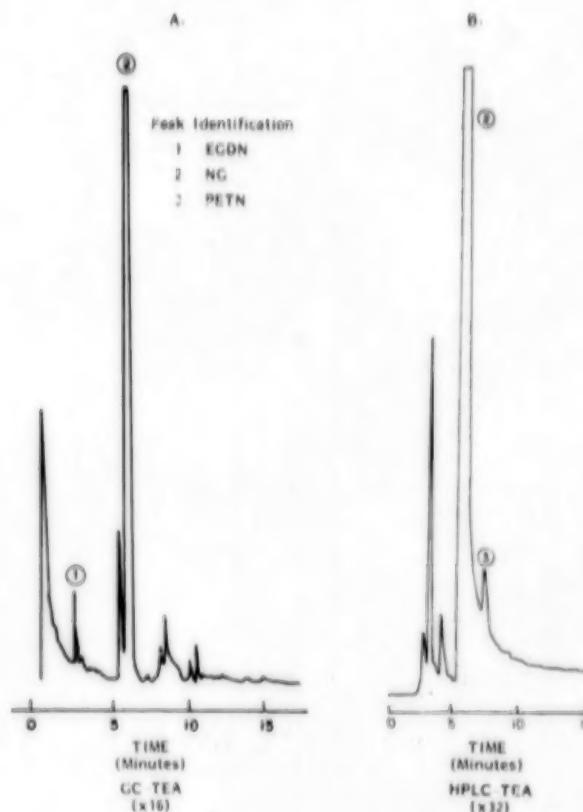


Figure 5. Chromatograms on GC-TEA and HPLC-TEA of an extract from post-explosion debris of a detonating cord bomb. On GC-TEA a 0.2  $\mu$ l injection of debris extract showed NG, and a trace of EGDN. On HPLC-TEA, a 5  $\mu$ l injection indicated NG, and a trace of PETN.

peak shape of PETN, which undergoes partial decomposition in the GC. Similarly, for the letter bomb, PETN was the only explosive that was detected on the hands.

Controlled experiments with handswabs that had been spiked with known amounts of explosives, indicated a lower detection limit of about 10 pg injected on column. Again, because of the selectivity of the detector, clean-up was not required.

#### CONCLUSION

The capability for routine detection of explosives at the low picogram level from 'real world' samples of military explosives, post-explosion debris, and handswabs, has been demonstrated. Because of the selectivity of the TEA analyzer, clean-up is not needed. The analytical methods are, therefore, simple and rapid. The minimum detectable amount for most explosives is 4-5 pg injected on column.

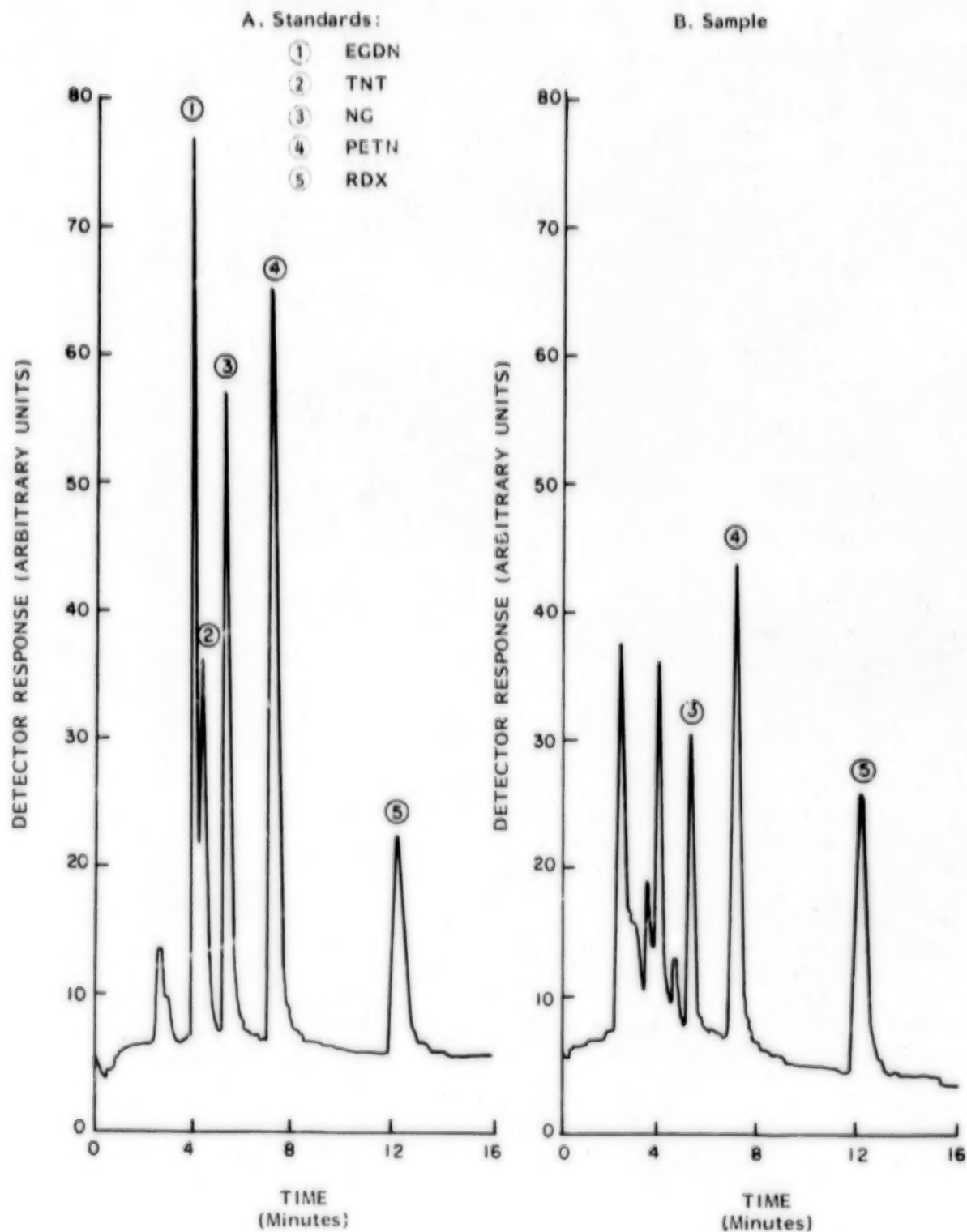


Figure 6. Chromatograms on HPLC-TEA ( $\times 16$ ) of 5 explosive standards (Figure 6A) and a 20  $\mu$ l injection of the extract from post explosion debris of a C4 bomb (Figure 6B). The peak identification is 1-EGDN, 2-TNT, 3-NG, 4-PETN and 5-RDX. The 20  $\mu$ l injection of debris extract contained 5 ng of NG, 6.8 ng of PETN and 9 ng of RDX.

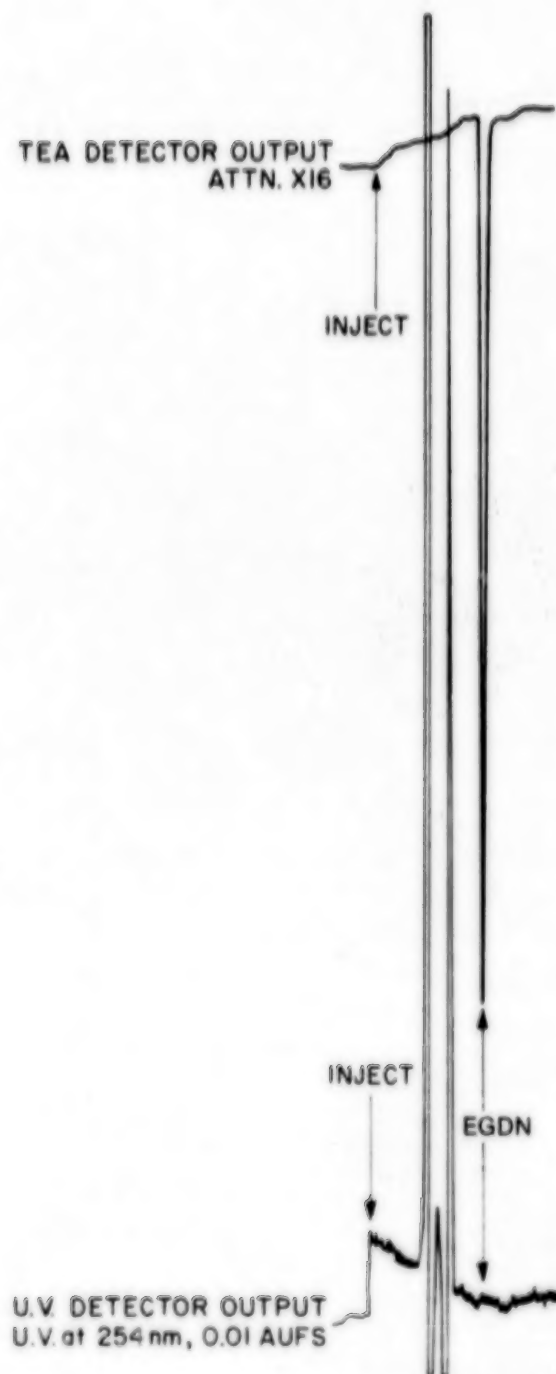


Figure 7. Chromatograms on HPLC-UV-TEA of an air sample which had been collected on a Thermosorb/N Cartridge, following a blast from a dynamite bomb. The 20 ul injection indicated the presence of 9 ng of EGDN.

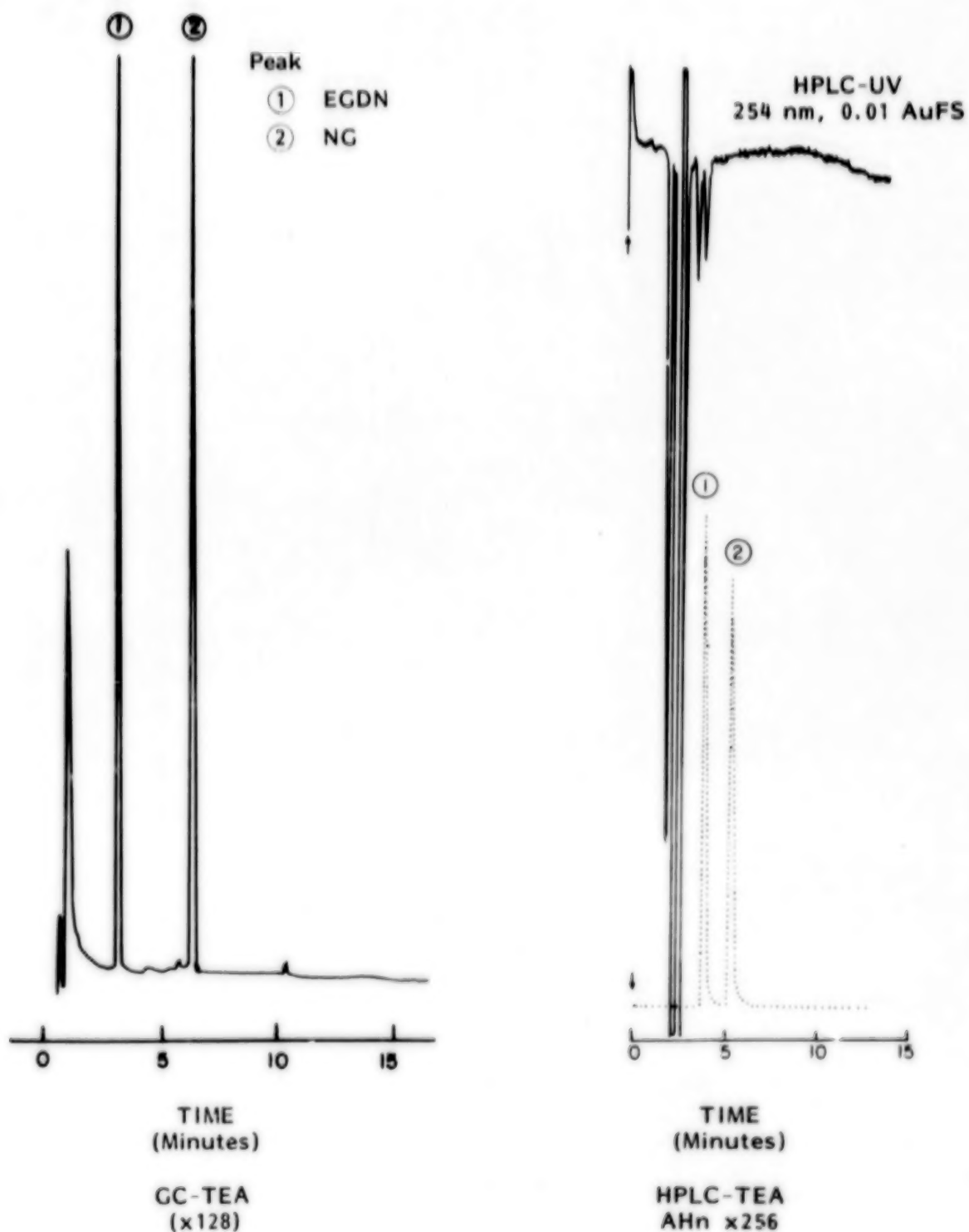


Figure 8. Chromatograms on GC-TEA and HPLC-UV-TEA of a gel dynamite handswab extract. The injection volume was 0.2  $\mu$ l on GC-TEA ( $\times 128$ ) and 1  $\mu$ l on HPLC-TEA ( $\times 256$ ). Peak 1 coeluted with EGDN, and peak 2 with NG.



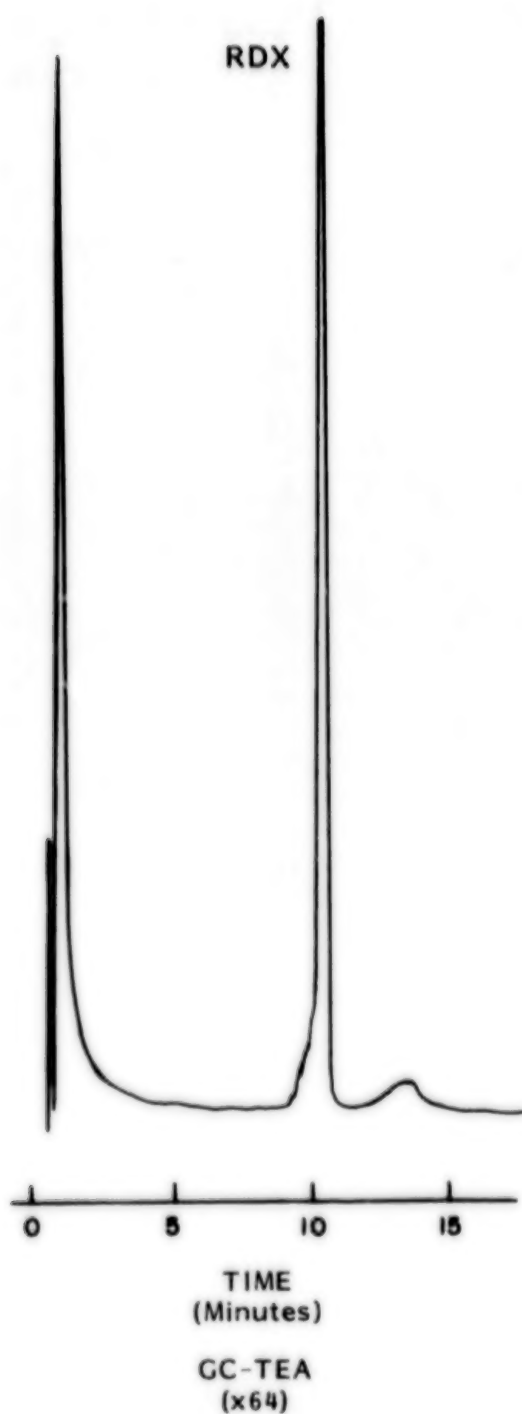


Figure 9. Chromatograms on GC-TEA and HPLC-UV-TEA of a C4 handswab extract. The injection volume was 0.3  $\mu$ l on GC-TEA ( $\times 64$ ) and 20  $\mu$ l on HPLC-TEA ( $\times 256$ ). Only a single major peak, due to RDX, was observed on both GC and HPLC.

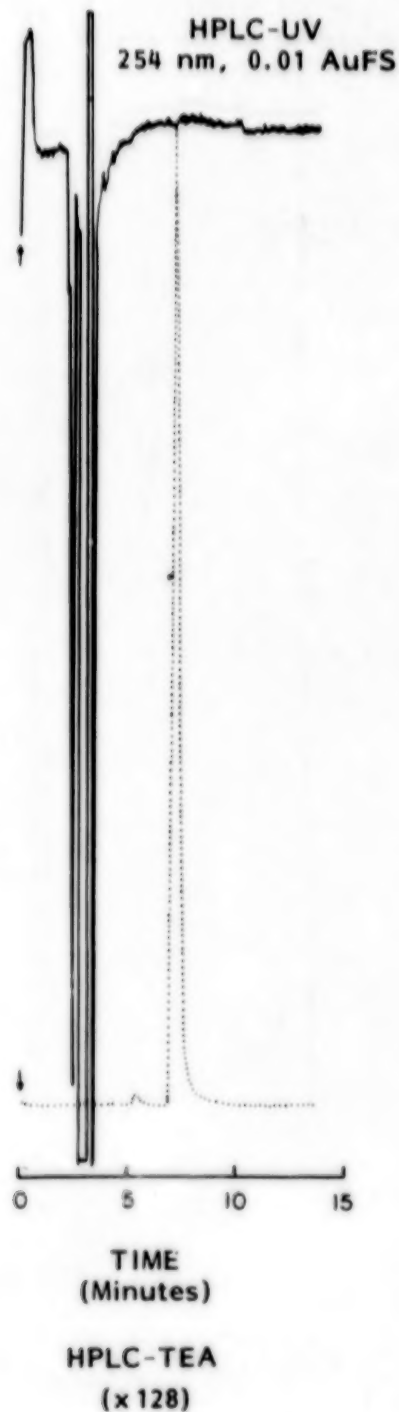
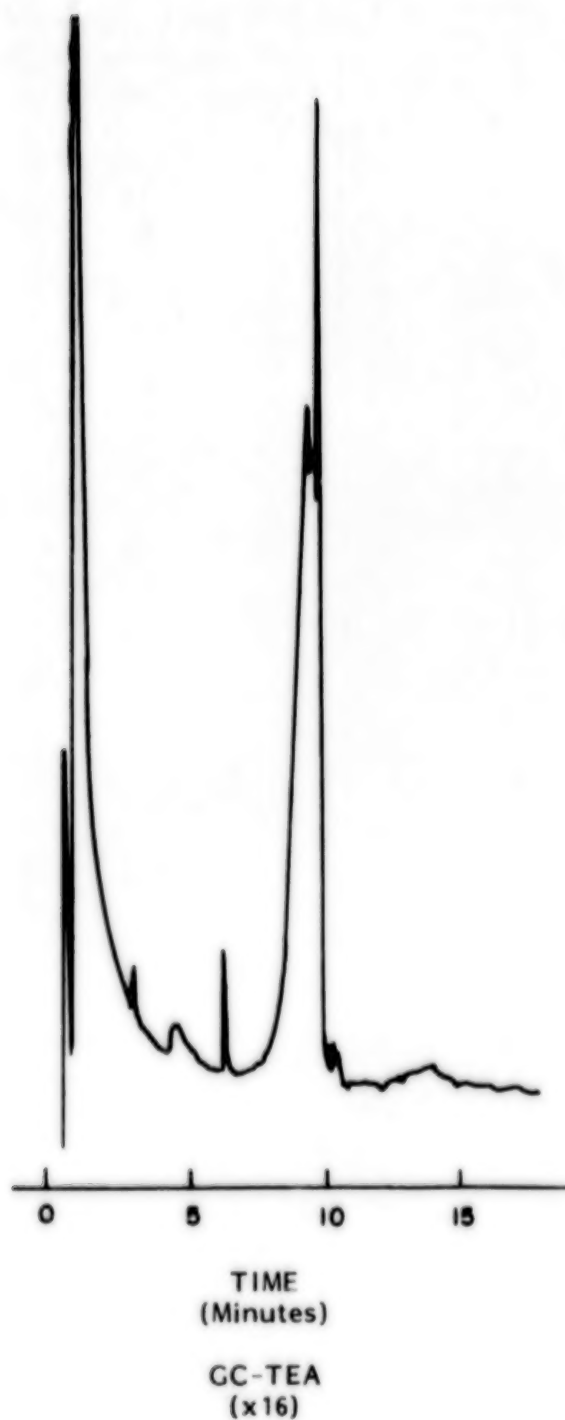


Figure 10. Chromatograms on GC-TEA and HPLC-UV-TEA of a handswab from a person who had handled a plastic explosive. On GC-TEA 0.4  $\mu$ l of the 2 ml extract was injected. A trace of NG (0.21 ng) and PETN was shown to be present (note the typical peak shape of PETN which decomposes on the column). For HPLC-TEA ( $\times 128$ ), 3  $\mu$ l was injected, giving a PETN peak due to 84 ng.

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# X-RAY PHOTOELECTRON SPECTROSCOPIC (XPS) DETECTION AND IDENTIFICATION OF EXPLOSIVES RESIDUES

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**ABSTRACT.** X-ray Photoelectron Spectroscopy (XPS) is a sensitive and powerful analytical technique with which residues in the nanogram range over an area of a square centimeter can be detected and identified. The 1s spectrum of nitrogen is particularly useful because the chemical shift of the nitrogen line distinguishes between the nitrate ester, nitro, nitroso and amine groups. The relative ratios of these groups in the debris can be determined and the explosive identified by the mode of molecular fragmentation. Combined with thin layer chromatography, XPS has proved to be a highly successful technique for forensic and malfunction investigations. Examples of specific applications are given.

## INTRODUCTION

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA) is now a well-established laboratory technique. It measures the binding energy of the electronic levels in a given sample. (Siegbahn *et al.* (1967), Brundle and Baker (1977)). The entire range of occupied electronic levels below 1000 eV binding energy is accessible to the XPS technique, giving it powerful analytical and research capabilities. Since the electronic level structure of any material is a reflection of its physical and chemical state, XPS has unravelled many metal, alloy, insulator, semiconductor, and catalyst problems. The technique has played a major role in surface physics due to its high sensitivity to the top surface layers of a solid.

In the field of explosives, the technique has been applied to study the electronic levels of primary and secondary explosives and the ingredients of rocket and gun propellants. This research has elucidated the different modes of molecular fragmentation caused in explosives by various stimuli such as shock, heat, and radiation. (Owens and Sharma (1979), Sharma *et al.* (1982)). As a by-product of this study, characteristic XPS spectra of explosives have been produced which can be used to identify explosives in forensic investigations of explosives residues. This paper will describe some applications of the XPS technique

to the detection and identification of explosives from the debris collected after an explosion. Some of the distinct advantages of the XPS technique will be pointed out.

## THE XPS TECHNIQUE

For XPS study, the specimen (typically 5 mm x 10 mm area) is irradiated with characteristic X-ray emission from a Mg anode (1253.6 eV) or Al anode (1486.6 eV) in a vacuum chamber. The ejected photoelectrons are energy analyzed in an electrostatic or electromagnetic analyser. From Einstein's photoelectric equation we have

$$h\nu = \frac{1}{2}mv^2 + E_b$$

The binding energy,  $E_b$  of the electronic level from which an electron is ejected, is determined from the known photon energy  $h\nu$  and the measured kinetic energy ( $\frac{1}{2}mv^2$ ). The data are usually plotted as the number of photoelectrons emitted as a function of binding energy. A full XPS spectrum displays peaks at all of the occupied electronic levels of the sample up to the energy of the exciting Mg or Al X-rays.

### a. Elemental Identification

Since all atoms possess a relatively small number of electronic levels (compared to the thousands of lines in optical spectra), the measurement of the core levels leads to a straightforward and unequivocal identification of the elements in a

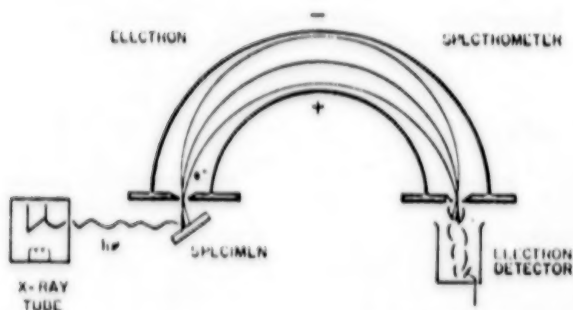


Figure 1. Schematic representation of the XPS measurement.

given sample. The core levels are also well-separated in relation to the resolving power of the instrument (1 eV). For example, the 1s levels of carbon, nitrogen and oxygen, three neighbors in the periodic table, are at approximately 285, 400 and 531 eV respectively. In the rare event of two lines from different atoms superimposing, one can verify easily by referring to other electronic levels of the atoms concerned. The atoms of higher atomic number have many electronic levels to mitigate this problem. A broad spectral scan from 0–1000 eV binding energy gives a full elemental analysis of the sample and the peak heights indicate the relative ratio of atoms in the specimen. Of course, one has to take into consideration the photoelectric cross-section of the different levels of the atoms. These are available from standard tables. The cross-sections over the periodic table vary only over a small range, (0.1–30) so that a wide scan provides us with a direct picture of relative concentrations. However, due to problems arising out of surface sensitivity of the technique, quantitative analysis is restricted to an accuracy of about ten percent.

#### b. Chemical Shift

The exact position of an XPS peak depends upon the oxidation state of the atom. Oxidation or partial loss of outer electrons moves the peaks to higher binding energy due to the effect of screening on core levels by the outer electronic orbitals. This chemical shift is often of the order of 10 eV and provides us with a powerful handle in the identification of explosives. For example, RDX and HMX give a pair of peaks, shown in Figure 2, at a characteristic separation of 5.7 eV, due to the different oxidation states of the amine and nitro nitrogen. The relative heights of the peaks are indicative of the ratio of the amine and nitro nitrogen in the molecule. RDX and HMX both show equal peaks because both of them have an equal number of nitro and amine nitrogens. When

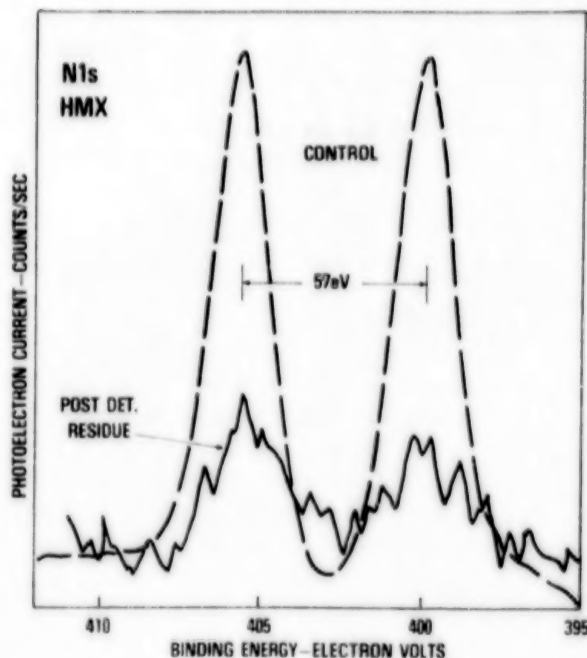


Figure 2. The N 1s spectrum of HMX and its post detonation residue, showing characteristics separation of 5.7 eV between the nitro  $\sim$  406 eV, and the amine  $\sim$  400 eV peaks.

explosives are degraded by radiation or heat, the changes in the molecules are also reflected by the nitrogen spectra.

The nitrogen of nitrate ester shows a maximum binding energy of 407 eV, the nitro appears at about 405 eV while the nitroso appears at about 402 eV. The amine nitrogen in most of the explosives is found to be at about 400 eV. This general pattern facilitates identification of explosives and their classes. Thus, XPS not only identifies the atoms in a given sample but it also gives information about the chemical environment of the atom. For determining the latter, a 20 – 30 eV wide scan is made in the region of the 1s electronic level of nitrogen.

#### c. Sensitivity of XPS

The kinetic energy of the photoelectrons on which the measurement of XPS is based is limited by the excitation energy (1253.6 or 1486.6 eV). Only electrons originating near the surface of the sample are capable of emerging and reaching the analyzer at these energies. Thus, the sampling depth of XPS is about 30 Å (six molecular layers) for organic materials while it is about half of that value or 15 Å for metals. This makes XPS very much a surface technique and sometimes the surface can be complicated and different from the bulk. On the other hand, since the whole signal is



originating in the top 30 Å of the sample, one can get full information from an infinitesimally small sample, provided it is well spread on the surface. Only  $10^{-8}$  gm. of a given sample is required for XPS studies. This feature makes the technique extremely sensitive. Detection of parts per billion from solutions have been reported by Brinen and McClure (1972) and even smaller levels have occasionally been detected. Brundle and Roberts (1972) have reported surface sensitivity of  $2 \times 10^{-3}$  atomic or molecular layer. In this respect XPS is one of the few techniques ideally suited for forensic detection and identification of explosives.

In the study of explosives by XPS the fact that nitrogen is a common constituent gives an advantage because this atom displays an appreciable chemical shift. The other advantage with nitrogen is that atmospheric nitrogen is inert and will not stick to surfaces as a contaminant. By contrast, oxygen and hydrocarbon are present on all surfaces as atmospheric adventitious impurities which can interfere with the interpretation of oxygen and carbon spectra of the sample. No such problem is posed by nitrogen.

#### CHARACTERISTIC EXPLOSIVES SPECTRA

Figure 3 shows the spectrum of lead azide; the nitrogen 1s and 4d levels of lead are exhibited. The azides show two nitrogen lines with a characteristic separation of 4.5 eV and in the ratio of 1:2 due to the positive and negative nitrogens in the azide ion  $\text{NNN}^-$ . The lower spectrum is that of lead azide partially decomposed by UV photolysis. Figure 4 shows the spectra of TNT (consisting of a single nitro peak), the spectrum of decomposed TNT and also the spectrum of explosion residue from TNT. The peak at 400 eV is due to the nitroso derivative of TNT invariably produced when TNT is decomposed in the solid, liquid or vapor phase, either by heat or by radiation. Figure 2 (lower curve) is the spectrum of explosion debris of HMX from a witness plate. Its similarity to the HMX (upper curve) spectrum is obvious. Unfortunately, due to the structural similarity between RDX and HMX, the XPS technique cannot distinguish between these two explosives. Figure 5 shows the N 1s spectra of (a) RDX control, (b) photolysed RDX, (c) thermally decomposed RDX and (d) explosion debris of RDX. The last spectrum shows a considerable amount of broadening to the higher binding energy side due to the generation of highly oxidized gaseous products sticking to the witness plate. Photolysis is found to cause a preferential

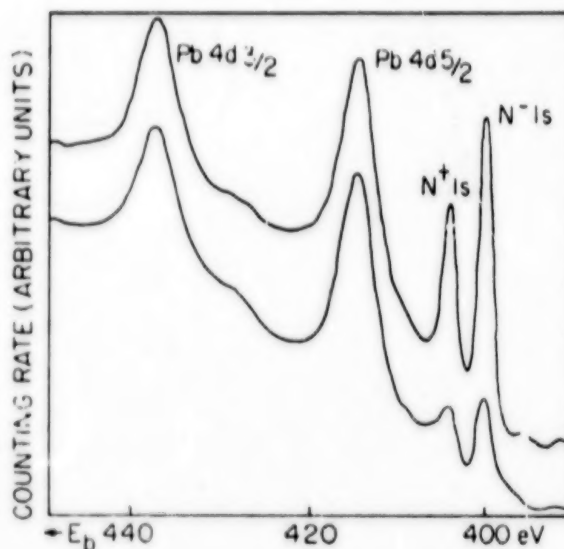


Figure 3. The N 1s spectrum of lead azide showing two lines of nitrogen in the ratio of 1:2 for the  $\text{N}^+$  and  $\text{N}^-$  in the azide ion. The lower spectrum is that of partially decomposed lead azide. The peaks at 415 and 436 eV are due to the d levels of lead.

decrease of the nitro line due to the separation of the nitro groups, while the amine group is not much affected. It appears (Figure 5 (c)) that thermal decomposition disrupts the whole molecule.

In the nitrate ester based explosives, such as PETN, NG and NC, the nitrogen peak shows up

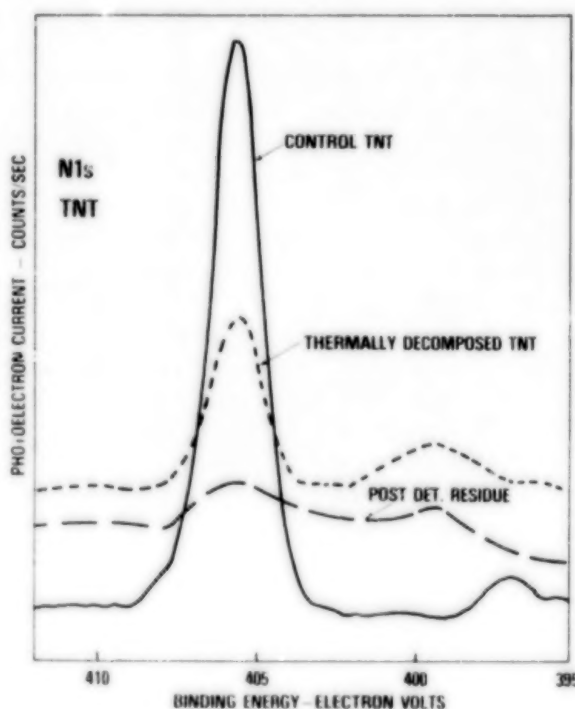


Figure 4. The N 1s spectrum of TNT, thermally decomposed TNT and post detonation residue of TNT.

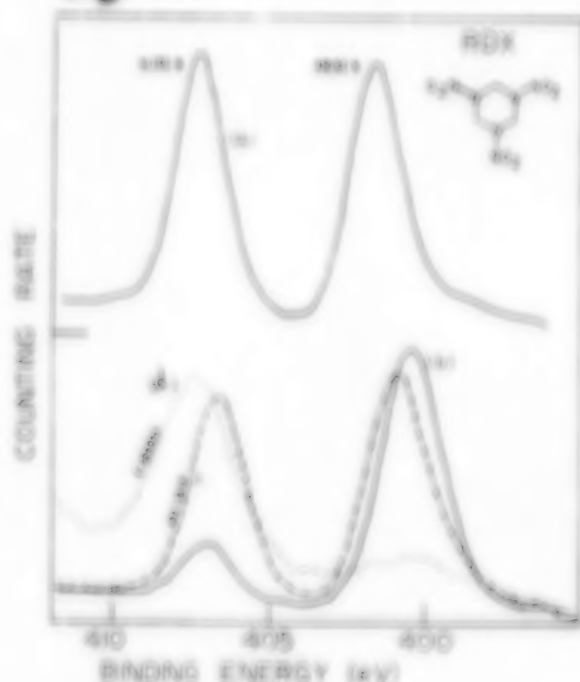


Figure 5. The N 1s spectrum of (a) RDX control, (b) photo-lysed RDX, (c) thermally decomposed RDX and (d) of explosion residue from RDX.

at 407 eV representing the highest oxidation state of the nitrogen. Figure 6 gives the N 1s spectrum of PETN along with that of its explosion residue. PETN shows some peaks in the nitro region when it is decomposed. This is evident in the above spectrum.

All of the spectra mentioned in this paper show that the 1s nitrogen spectra of residues in the range of 410-395 eV can help in the detection and identification of explosives. Even in the case of a high order detonation, at least a fractional percent of the original explosive will be scattered without full destruction, and can stick to the surrounding area. Consequently, if swabs and debris are collected from the area of an explosion, XPS analysis combined with other techniques can lead to a successful investigation. XPS has also been used in many successful investigations of weapon malfunction, where it played an especially critical role in distinguishing between the areas exposed to explosives and ones exposed to propellant.

A few concrete cases of investigations in which XPS has been of critical help are mentioned in the following.

#### CASE STUDIES

A number of empty, new steel shells were being heat treated for improving their fragmentation

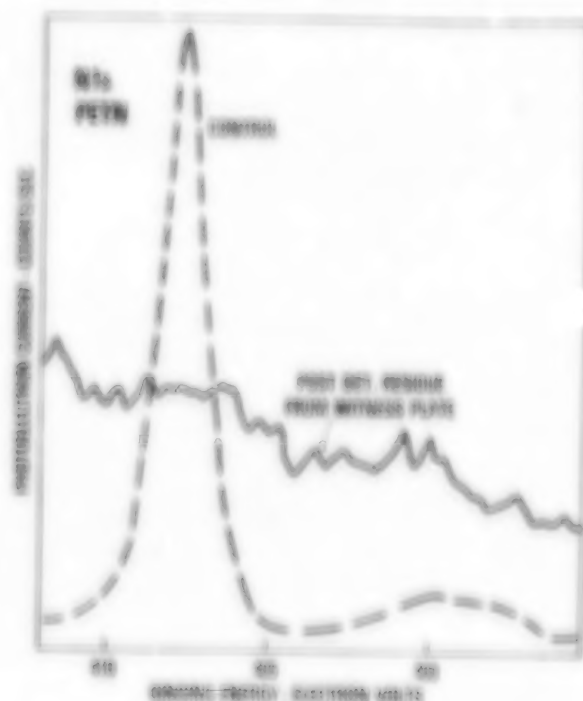


Figure 6. The N 1s spectrum of PETN, showing peak at 407 eV, and that of its explosion residue showing broadening towards higher binding energy due to deposition of nitrogen oxide vapors on the witness plate. Some nitro products also show up at 407 eV.

process. One of them exploded during heating causing serious damage to the furnace and the laboratory. Only XPS study of the inside wall of the exploded shell showed evidence of TNT and its thermally evolved products. Subsequent tests by conventional methods on samples collected from the same lot of shells confirmed the presence of TNT. It turned out that the vendor had supplied used shells which had been cleaned with steam. Obviously some shells had escaped a thorough cleaning and had caused the explosion.

A fatal explosion was being investigated. In the area of the explosion, a large amount of fertilizer consisting of ammonium phosphate and sulfate was blown up which made analysis of the residue extremely difficult. Only XPS study, Figure 7, showed separate peaks due to the ammonium and the nitrate ester nitrogen leading to the identification of nitroglycerine. In this study, the investigation was successful because XPS could detect the two kinds of nitrogen in the strong background of the fertilizer. Once it was known that a nitrate based explosive was involved, TLC and mass spectrometry confirmed NG.

In still another investigation, an explosion had taken place in lockers, located under automatic

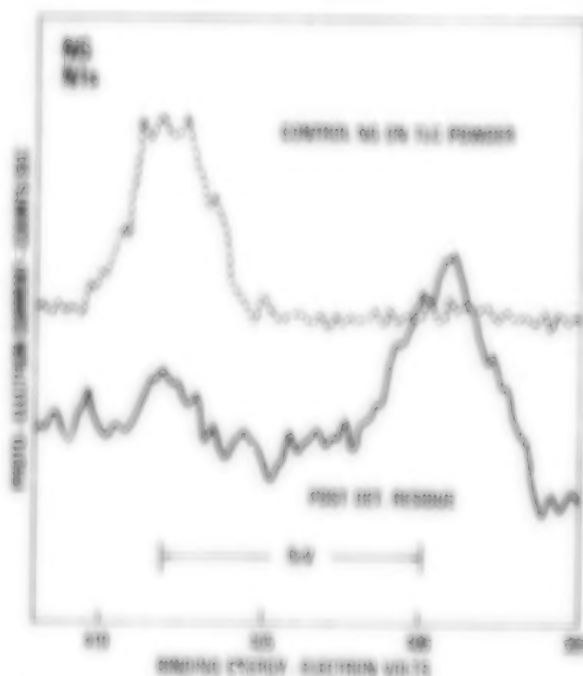


Figure 7. The upper curve is the N 1s spectrum of NO on TLC powder obtained at  $-70^{\circ}\text{C}$ . The lower spectrum is that of post-decomposition residue, showing NO peak at 407 eV distinct from that of N in ammonium sulfate or ammonium phosphate.

sprinklers. The explosion caused the sprinklers to operate, and the site was under two inches of water, before an investigator could arrive. All the evidence of the explosives had been washed away and conventional methods of investigation failed to give any clue. XPS examination of the deformed locker surfaces and their scrapings identified standard dynamite to be the explosive used. Of course, once the clue had been given by XPS, it was possible to confirm the finding by TLC and mass spectrometry. In such investigations, one looks for the spectra of both the explosive and its

decomposition products.

In summary, XPS is an analytical technique which, along with other methods of analysis, can be exceedingly helpful in forensic investigations.

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# CHARACTERIZATION AND IDENTIFICATION OF WATER SOLUBLE EXPLOSIVES

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**ABSTRACT.** This paper describes a simple technique whereby water soluble inorganic explosive compounds are characterized by their crystal shape, size, and interfacial angles as they recrystallize from a drop of water on a microscope slide. Once the crystals are characterized, the inorganic explosive compound(s) can be confirmed by other optical properties and such as refractive indices, extinction angles, and birefringence, and/or by conducting microchemical tests. The advantage of this procedure is that it is fast, inexpensive, only a minute amount of sample is needed, and does not require a broad knowledge of optical crystallography. A discussion of the characteristic crystals and the identification of the common inorganic explosive compounds will be presented. The application of the technique to cases received in the laboratory will be demonstrated.

## INTRODUCTION

Forensic laboratories are often faced with the task of analyzing and identifying explosive compositions. This type of evidence may be submitted as intact mixtures or as residue collected at a bombing scene. Usually the analysis involves identifying the explosive component which may include one or more of the water soluble inorganic compounds (oxidizers) that are present in black powders, pyrotechnic mixtures, and in some high explosives.

There are published methods for the systematic analysis and instrumental identification of the inorganic explosives of these explosives. The main disadvantages to these techniques are that they normally require large samples, specialized instrumentation, are time-consuming, and may only give an indication as to the inorganic oxidizer present.

A method for identifying high explosives by looking at profile angles and correlating this data with other crystal properties has been described by McCrone. (7). This paper described a similar approach to the identification of the water soluble

inorganic explosives. As with the identification of the high explosives, this method has the advantages of speed, simplicity, small sample size (normally less than 1 mg.) and is inexpensive.

Characteristic crystal forms are described for each of the ten explosives along with other crystal data to aid in quick identification. Crystal descriptions that are in italics are considered by the authors to be somewhat peculiar to that compound. Photomicrographs and diagrams have been included to aid in a better understanding of the description of the crystals. All photomicrographs were taken at the same magnification (100x), with polarized light, as the compounds recrystallized from a drop of water. Therefore, the photomicrographs are indicative of the relative relief and crystal size that should be observed.

## PROCEDURE

The particles to be studied can best be isolated by physical removal with fine forceps or needles under the stereo-binocular microscope. Water extraction may be used but could lead to metathetical reactions if several compounds are present.

These techniques have already been well covered by previous works to which one should refer for further information. (1,4,5,8,14,17).

If the particle is physically removed, the following procedure is followed:

1. By means of a glass rod that has been drawn out to one end to a 1 mm tip, place a small drop of distilled water 5mm to 7mm in diameter in the center of a clean microscope slide.

2. Add the particle to be investigated into the droplet. For all but the very soluble ammonium nitrate, the size particle need not be any larger than the hole in the letter "b."

3. Crush the crystal in the drop with the drawn-out glass tip being careful not to spread the drop. It is very important to observe only crystals that grow entirely submerged; dry crystals are badly misformed and much less characteristic. Continue crushing the crystals to reduce their size and to stir the drop thus aiding dissolution.

4. Any crust that develops at the edge of the drop should be pushed into the center being careful not to spread the drop.

5. Continue as above until well-formed crystals in the drop begin to grow.

If a water extract has been conducted (on the evidence under investigation), the extract should be evaporated to a small volume and a drop of the extract transferred to a microscope slide. Proceed with Step 4 as described above. Successive droplets may be evaporated on the same spot to increase the amounts of solute. This will ensure well-formed crystals before the droplet goes dry.

Once the crystals are characterized, one can confirm the identity of the compounds by utilizing other crystal properties (i.e. refractive index, melting points, interference figures, etc.), and/or by conducting microchemical tests. This can easily be done by redissolving the droplet and splitting it into several fractions or by physically removing the crystals from the dried residue. Microchemical tests and optical data are listed in the attached Appendices.

## CHARACTERIZATION

### Nitrate Compounds:

**Barium Nitrate** [ $\text{Ba}(\text{NO}_3)_2$ ]. This compound is only slightly soluble in water and crystals form at the edge of the droplet almost immediately. These should be pushed back into the center of the drop. Cubes, well formed octahedra, and recognizable combinations and distortions thereof soon appear. Crystals having 60° angles lie on octahedral

faces; those on cube faces show 120° angles. These crystals are isotropic and show moderate relief in water. (Figure 1).

**Potassium Nitrate** [ $\text{KNO}_3$ ]. At first, as the droplet evaporates, crystals consisting mainly of ill-formed rhombs and chevrons of "L's" form at the very edge, break away, float out to the center of the drop, and redissolve. As the droplet nears dryness, the crystals consist of well-formed and ill-formed rhombs, distorted bipyramids, prisms, blades, and rods. These crystals have high retardation colors. The prisms and rhombs are usually so ill-formed that accurate interfacial angles are difficult to measure. However, the acute angle of the rhombs is 77°, the obtuse angle is 103°. The prisms have angles of 80° and 140°. (Figure 2).

**Ammonium Nitrate** [ $\text{NH}_4\text{NO}_3$ ]. This compound is very soluble; additional sample and a smaller original droplet will help recrystallization. With care, it is possible to obtain thin rods, blades, ill-formed prisms, tablets and bipyramids. Very gentle warming may help (35-45° C). These crystals have high to very high retardation colors, depending on the crystal thickness. Ammonium nitrate is very deliquescent and if high humidity conditions exist, will pick up moisture and redissolve. (Figure 3).

**Sodium Nitrate** [ $\text{NaNO}_3$ ]. Sodium nitrate is also very soluble though not as soluble as  $\text{NH}_4\text{NO}_3$ . Enough solute should be added to saturate the drop before it gets too small and flat. The drop almost completely evaporates before any crystals appear. A crust may develop which consists of pointed twins and ill-formed rhombs which should be pushed back into the drop. Numerous well-formed rhombs soon appear and a few plates and tablets may develop. These rhombs have interfacial angles of 77° and 103°. The rhombs have very high retardation colors. (Figure 4).

**Lead Nitrate** [ $\text{Pb}(\text{NO}_3)_2$ ]. Recrystallizes from water as well formed cubes, octahedra, and recognizable combinations and distortions thereof. These cubic crystals have very high relief in water. (Figure 5).

All of the compounds of the nitrate group are easily identified by their unique crystal forms and optical properties. The microchemical tests for both the cations and anions are straight forward and should not cause any problems. Barium nitrate and lead nitrate have similar crystal shapes but the difference in their relief in water should distinguish the two.



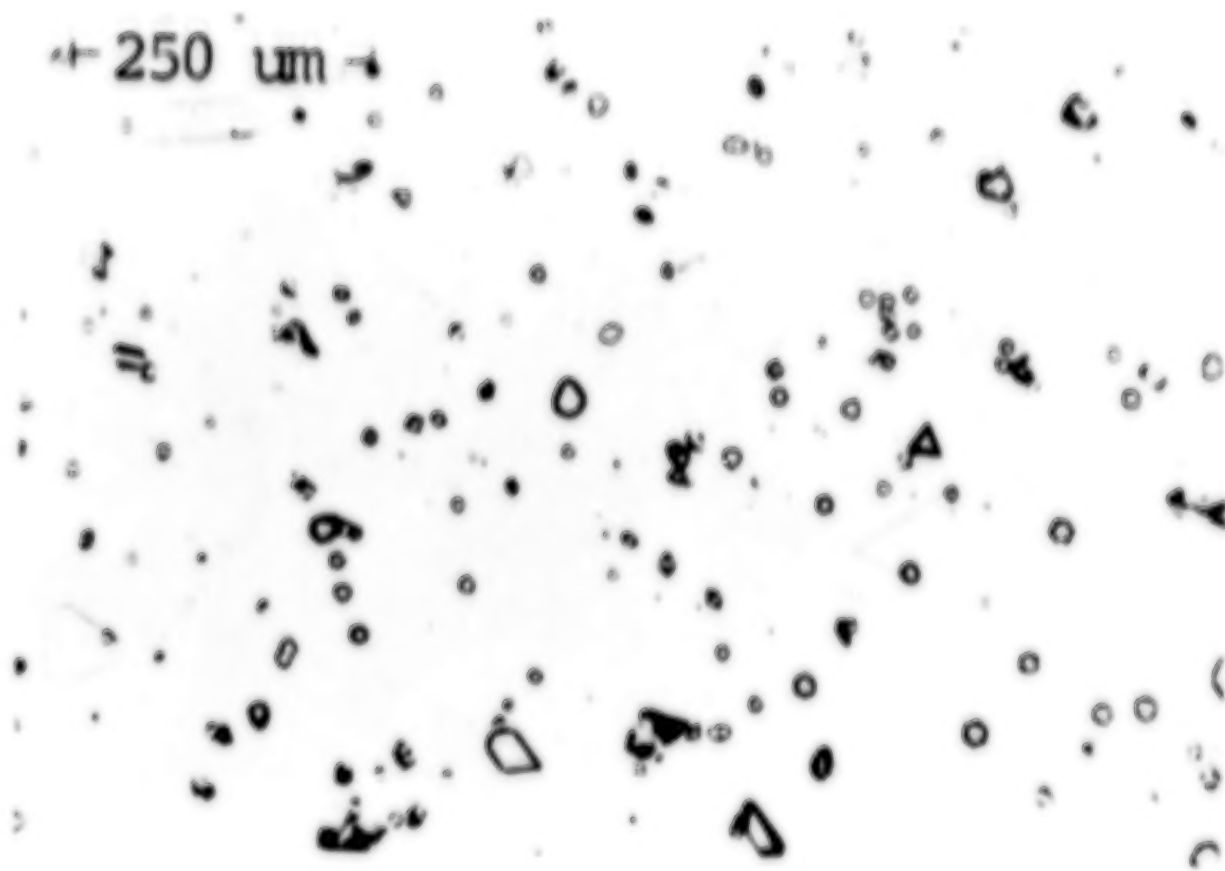


Figure 1. Octahedra and cubes of barium nitrate recrystallizing from water. (100x)

#### Perchlorate Compounds:

**Ammonium Perchlorate** [ $\text{NH}_4\text{ClO}_4$ ]. As the drop goes to dryness, two types of crystals develop; a set of two prisms and one or more pinacoid views. The latter show  $90^\circ$  angles, the prism views are 6-sided and show angles of  $135^\circ$ ,  $90^\circ$ ,  $135^\circ$  or  $117^\circ$ . It is not necessary to observe all of these forms to be sure of the presence of  $\text{NH}_4\text{ClO}_4$ . These crystals are orthorhombic and show low retardation colors. (Figure 6).

**Potassium Perchlorate** [ $\text{KClO}_4$ ]. This compound is slightly soluble and small, well-formed crystals immediately appear. These crystals consist of equant to rectangular prisms, rhombs, prisms (and distortions thereof) and pointed prisms where the tips may be truncated. The crystals show only low order retardation colors. (Figure 7).

**Sodium Perchlorate** [ $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$ ]. Sodium perchlorate crystals do not like to form as the droplet evaporates unless a little undissolved hydrate is left in the droplet. Also, like ammonium nitrate, gentle warming may help ( $35^\circ$ - $40^\circ\text{C}$ ). If this is the case, you will form diamond shape

rhombs of the dihydrate. These crystals may become very large in size. The interfacial rhomb angles are  $38^\circ$  and  $142^\circ$ . Low to medium retardation colors are observed for these crystals. (Figure 8).

The perchlorates can easily be identified and confirmed by characteristic shapes, optical properties, and microchemical tests. Even though sodium perchlorate may cause some difficulty at first, its crystal habits are characteristic and should not cause any problems.

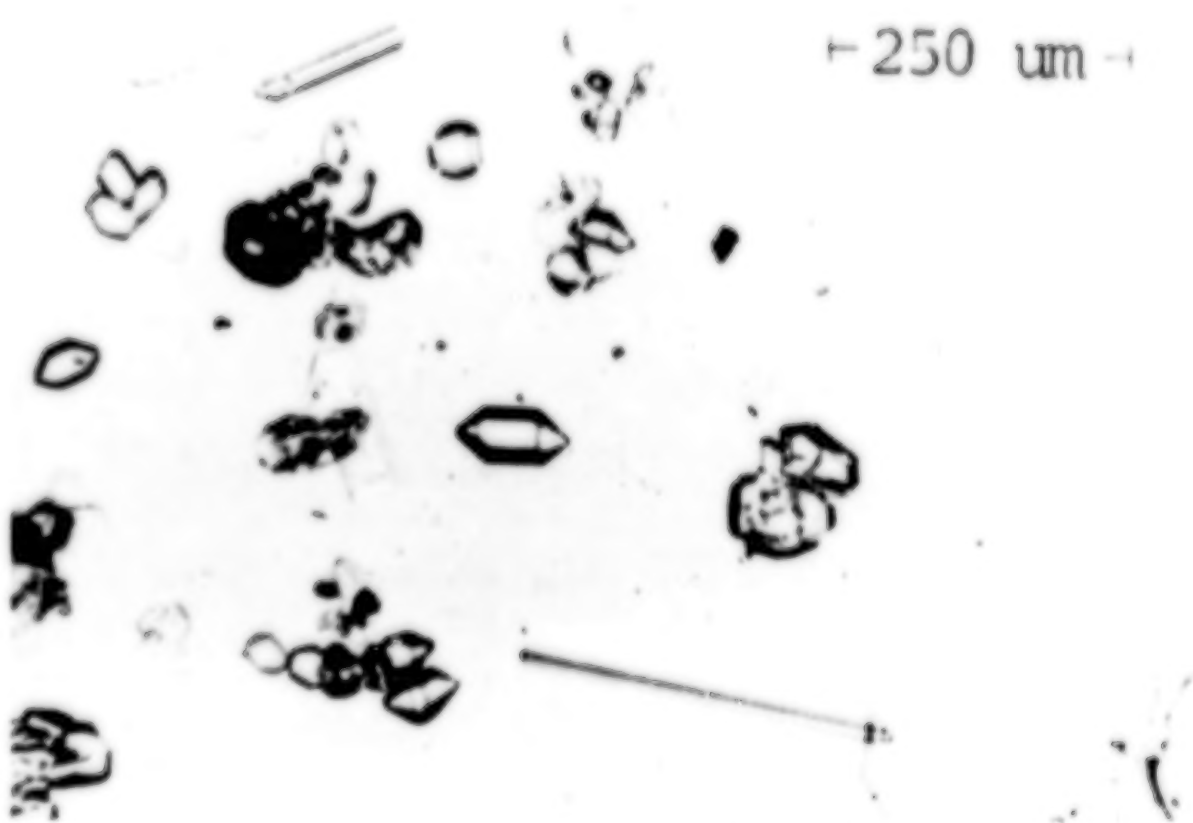
#### Chlorate Compounds

**Potassium Chlorate** [ $\text{KClO}_3$ ]. As a drop evaporates, a crust may develop consisting of aggregates of partially formed rhombohedra and should be pushed back into the drop. Inside the drop well-formed platy parallelograms (thin rhombs) and small well-formed rhombs develop. These have interfacial angles of  $80^\circ$  and  $100^\circ$ , medium retardation and symmetrical extinction. (Figure 9). Also, prisms and octahedra may also develop.

**Sodium Chlorate** [ $\text{NaClO}_3$ ]. This compound is very soluble and the droplet goes to near dryness before any crystals develop. However, once re-



← 250  $\mu\text{m}$  →



← 250  $\mu\text{m}$  →

Figure 2. (A) Chevrons and rhombs of potassium nitrate recrystallizing from water. (100x) (B) Rods and prisms of potassium nitrate recrystallizing from water.



Figure 3. Rods and bipyramids of ammonium nitrate recrystallizing from water. (100x)

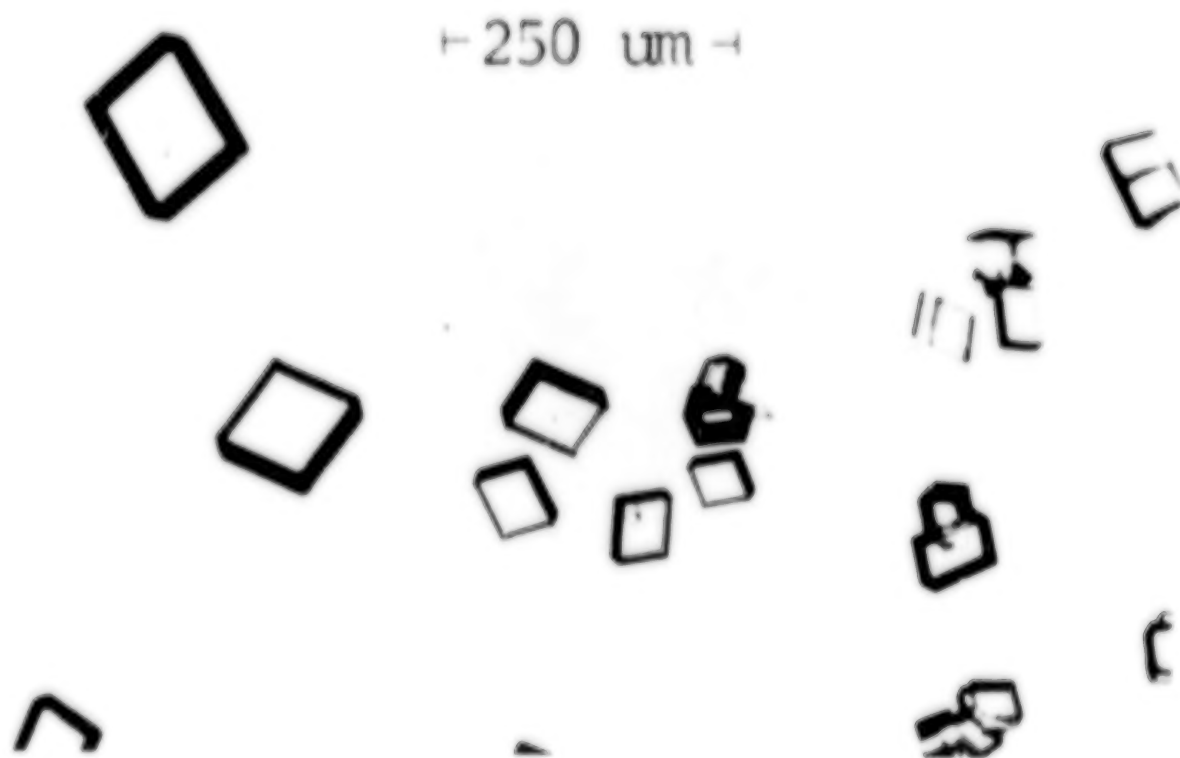


Figure 4. Rhombs of sodium nitrate recrystallizing from water. (100x)

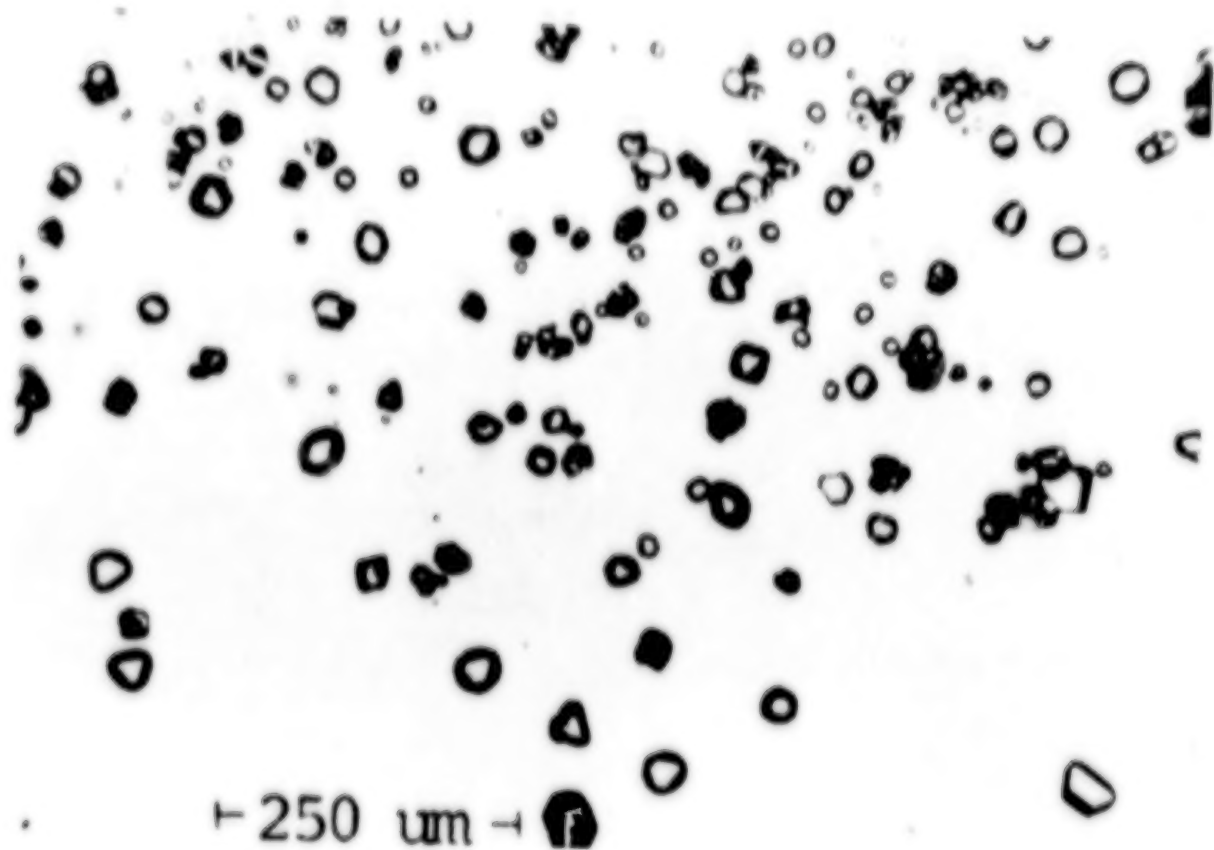


Figure 5. Cubes and octahedra of lead nitrate recrystallizing from water. (100x)

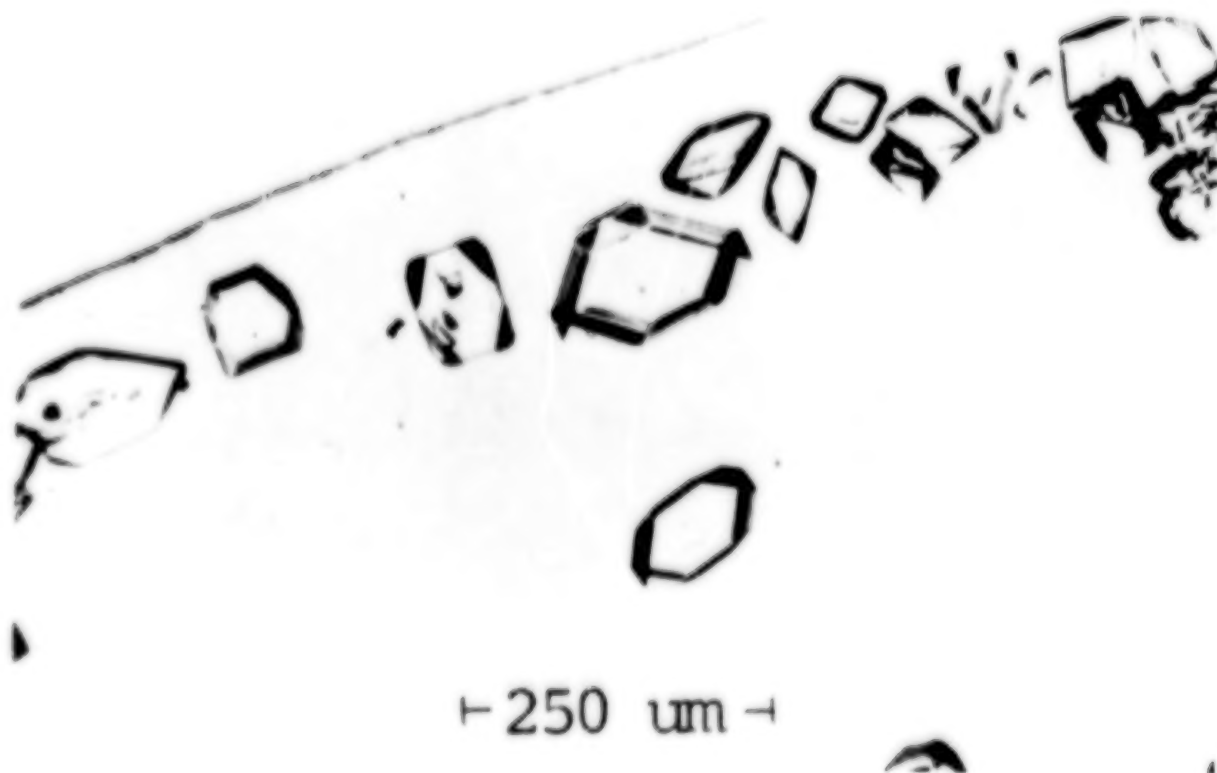


Figure 6. Prisms of ammonium perchlorate recrystallizing from water. (100x)

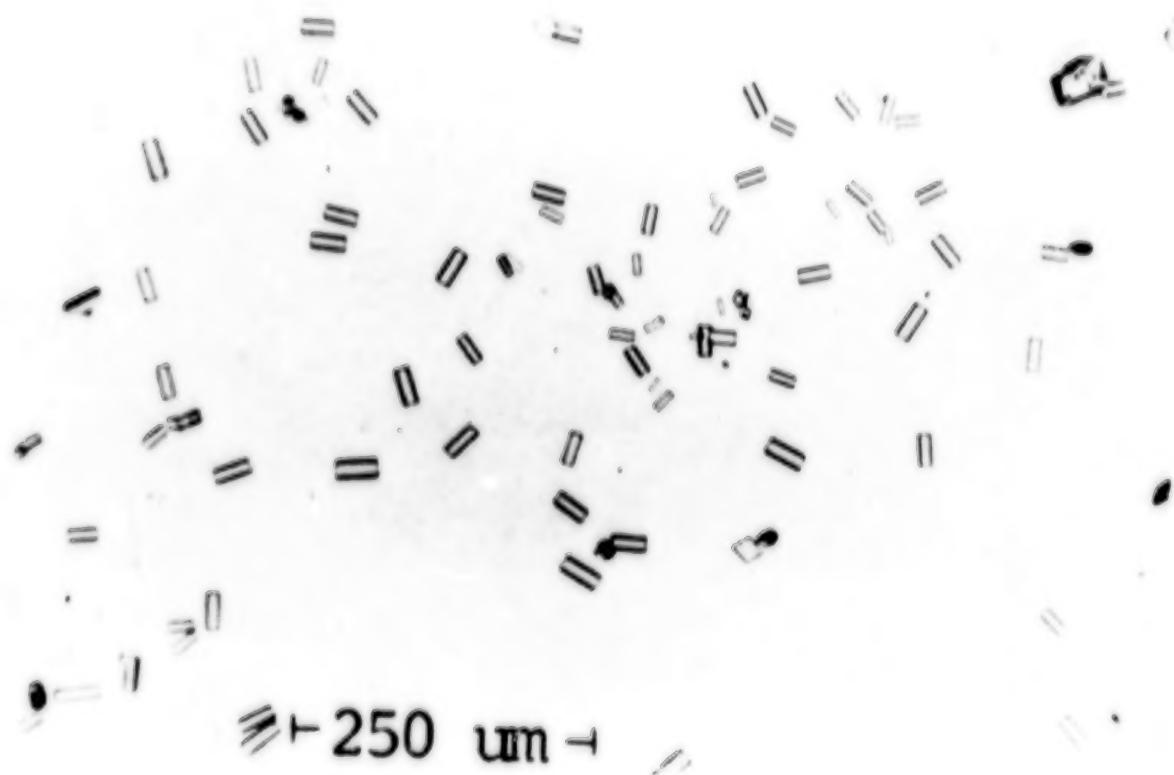


Figure 7. Prisms of potassium perchlorate recrystallizing from water. (100x)

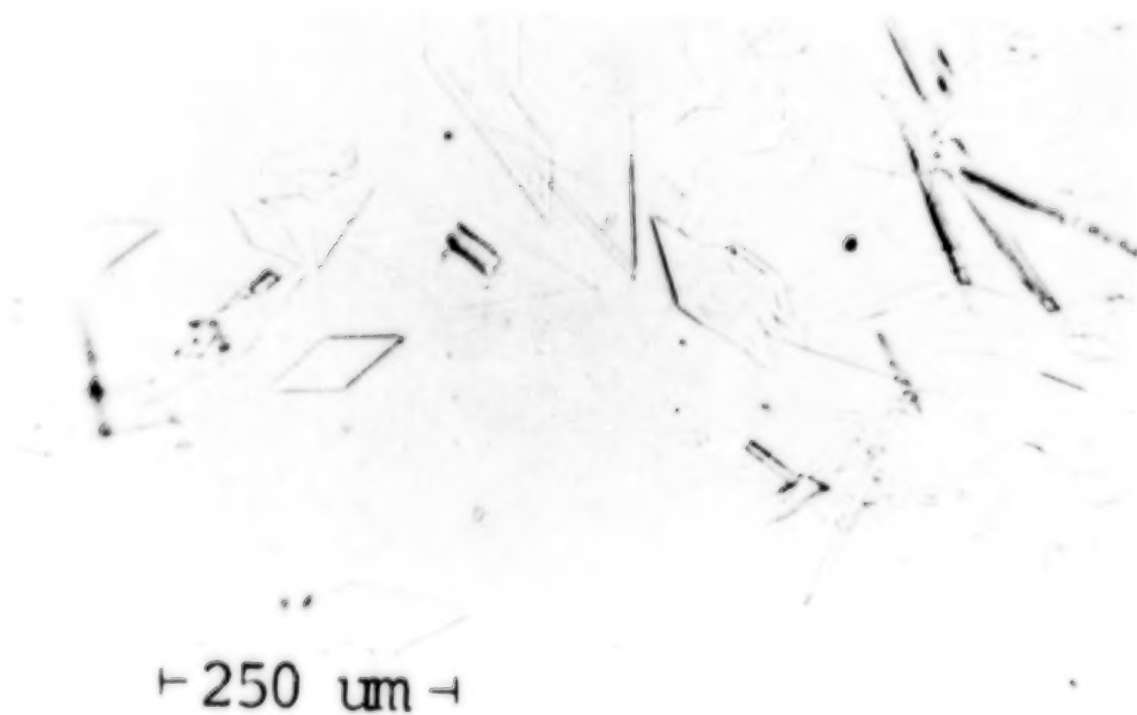


Figure 8. Diamond shaped rhombs of sodium perchlorate dihydrate recrystallizing from water. (100x)

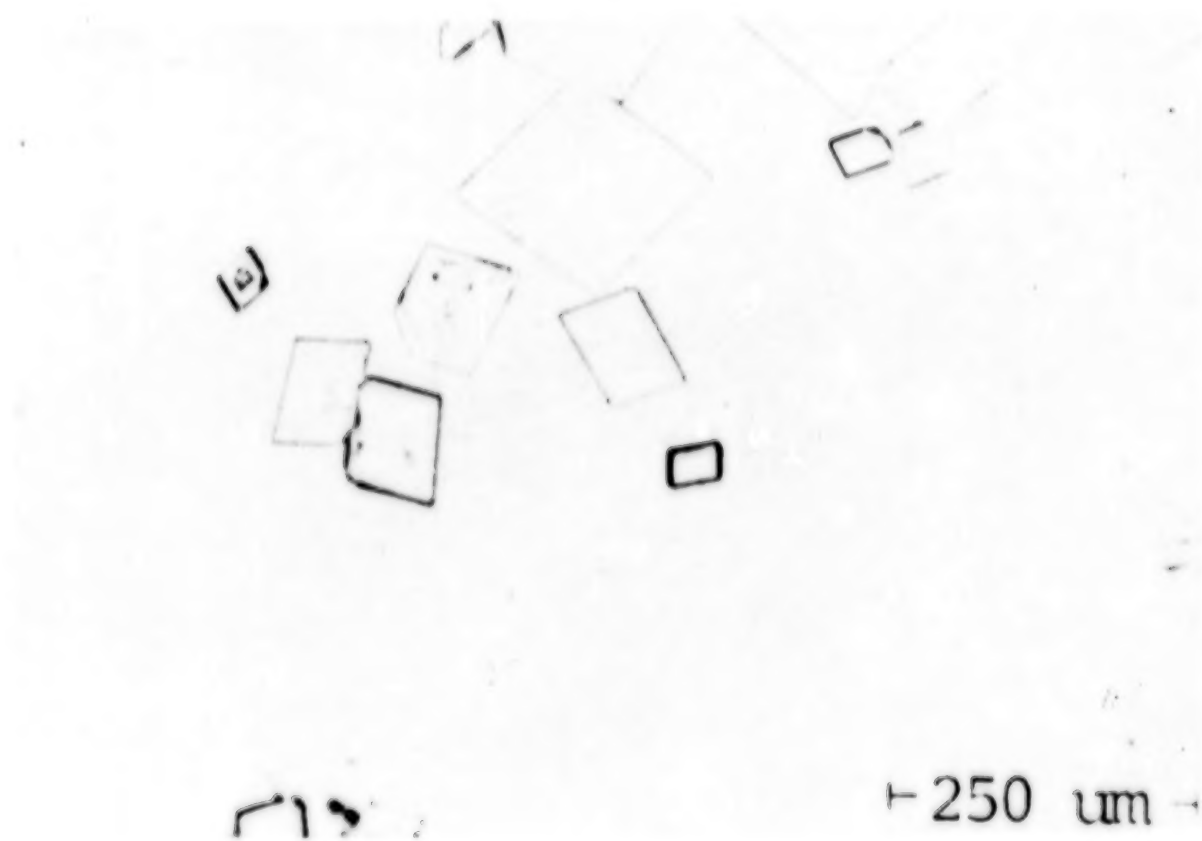


Figure 9. Rhombs of potassium chlorate recrystallizing from water. (100x)

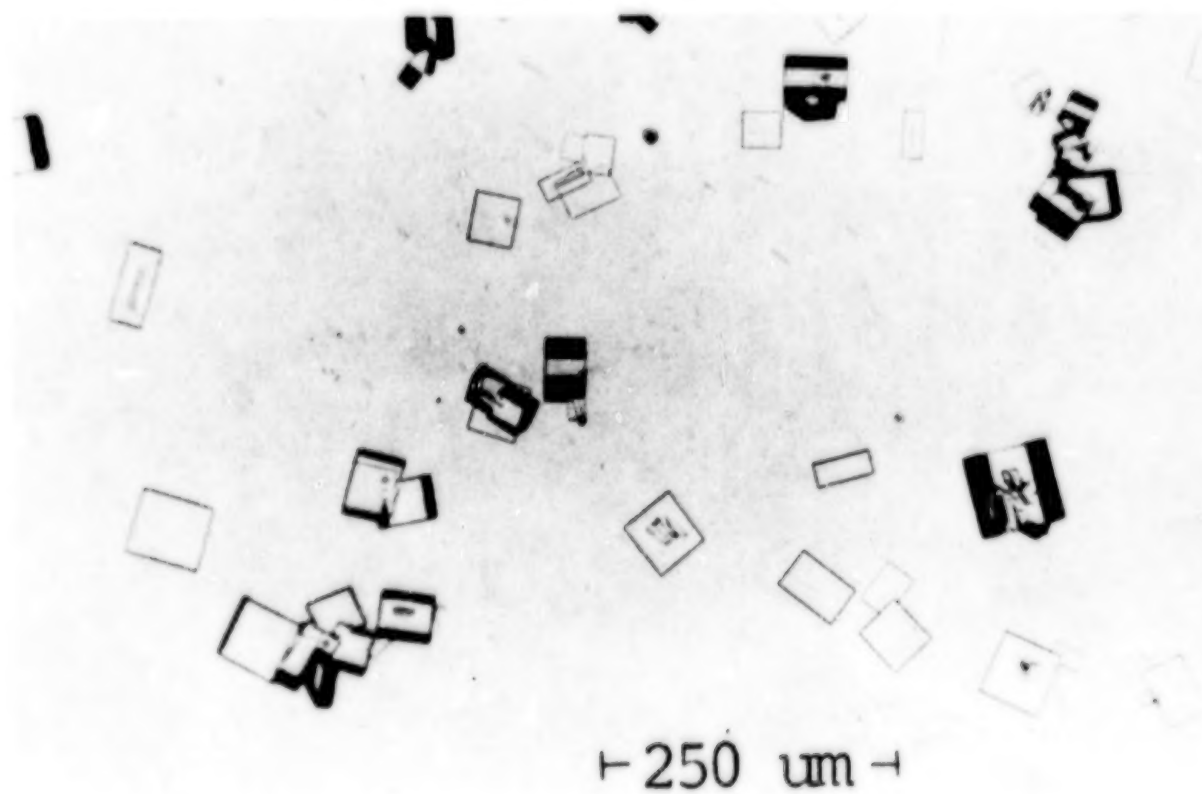


Figure 10. Cubes of sodium chlorate recrystallizing from water. (100x)



crystallization starts, it is spontaneous and the droplet is filled with masses of *squares, rectangles*, thin rods, well-formed and distorted octahedra. *Twinned crystals* are common. Sodium chlorate is cubic. (Figure 10).

The characterization of the chlorate compounds should not cause any problem. The microchemical tests for the cations are considered specific but this does not hold true for the chlorate anion since it does not form any insoluble crystals. A color microchemical test is included in Appendix I but is not considered specific for chlorates.

## DISCUSSION

Sodium nitrate, potassium chlorate, and potassium perchlorate form somewhat similar shapes but can easily be distinguished by their respective retardation colors (high, moderate, and low respectively). Also, distinguishing lead nitrate from barium nitrate is made easy by the fact that lead nitrate has a higher refractive index and therefore, has higher relief in water. Ammonium nitrate and sodium perchlorate may cause some difficulties at first, but with a little practice, these are easily overcome. Figure 11 lists some characteristic crystal forms and optical data that can be used for identification.

## WATER SOLUBLE EXPLOSIVES

(Under polarized and crossed polarized light)

### Compound

#### ISOTROPIC

$\text{Ba}(\text{NO}_3)_2$ ,  $n = 1.571$ , cubes, pointed tablets, octahedra. (Medium relief in  $\text{H}_2\text{O}$ )

$\text{Pb}(\text{NO}_3)_2$ ,  $n = 1.781$ , cubes, pointed tablets, octahedra. (High relief in  $\text{H}_2\text{O}$ )

$\text{NaClO}_3$ ,  $n = 1.518$ , squares, rectangles, square-ended prisms. (Twinning is common)

#### LOW BIREFRINGENCE

$\text{NH}_4\text{ClO}_4$ ,  $n's = 1.482-1.488$ , well formed prisms of two types.

$\text{KClO}_4$ ,  $n's = 1.473-1.477$ , rectangular prisms, rhombs.

#### MEDIUM BIREFRINGENCE

$\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$ , diamond shaped rhombs. (Only appear if undissolved crystals of the hydrate is present)

$\text{KClO}_3$ ,  $n's = 1.415-1.523$ , well formed rhombs.

#### HIGH BIREFRINGENCE

$\text{NaNO}_3$ ,  $n's = 1.336-1.587$ , well formed rhombs.

$\text{KNO}_3$ ,  $n's = 1.335-1.506$ , rhombs, prisms, chevrons (or "L's") (usually ill formed).

$\text{NH}_4\text{NO}_3$ ,  $n's = 1.413-1.637$ , rods, blades, ill-formed bipyramids.

The procedure has been performed on cases that were submitted to the laboratory for analyses with several examples listed below. The procedure used to separate the oxidizer include physical removal and water extraction.

### Case Example 1:

Several types of high explosive materials were submitted for analyses. These included water-gels, extra gelatin dynamites, and straight dynamites. The inorganic oxidizer was isolated by "particle picking." Ammonium nitrate and sodium nitrate were identified in their respective dynamites without any difficulty.

### Case Example 2:

An aluminum powder was submitted to determine if it were a pyrotechnic mixture. Macroscopic examination revealed a fine powder adhered to the surface of the aluminum flakes but were too small for particle picking. Crystals from a droplet of the water extract were identified as sodium nitrate.

### Case Example 3:

A tan powder was submitted to determine if it were an explosive mixture. A water extract was conducted and a mixture of potassium chlorate and potassium perchlorate was identified. (Also quartz and sulfur were identified by other microscopic procedures.)

### Case Example 4:

A white powder was submitted to determine if it was a pyrotechnic compound. Potassium perchlorate, potassium nitrate, and barium nitrate were identified utilizing this procedure. (Also, starch, diatoms, and strontium nitrate were identified by other microscopic techniques.)

## SUMMARY

This procedure provides a quick, inexpensive, and easy method for the identification of inorganic compounds (oxidizers) that may be encountered in high explosives, in flash powders, or as residue from a bombing scene. There is no problem in distinguishing any of the compounds from each other, whether in the pure state or in a mixture. Practicing first with knowns, it will save hours in analytical time in the long run. Even if instrumental methods are used to confirm the identification, it would still save sample preparation

and analysis time by not requiring that non-explosive compounds be analyzed.

### ACKNOWLEDGEMENTS

A special "Thanks" to Dr. W. C. McCrone, Dr. Richard A. Roper, Ms. Barbara Blaylock, and Mrs. Michelle Sloan for their patience and help in preparing this manuscript.

### APPENDIX I

Microchemical tests provide a very quick and simple means of confirming the presence of inorganic ions. For a more comprehensive overview of the topic, one should refer to the literature (11-13). The microchemical tests that are needed to confirm the presence of the cations and anions listed in this paper are described.

#### Sodium ( $\text{Na}^+$ ).

Dissolve the sample to be tested in a small drop of water. Near this drop (but not touching) dissolve a few crystals of zinc acetate and uranyl acetate in a drop of water acidified with acetic acid. Draw the reagent drop toward the drop to be tested until they meet. Characteristic octahedra will appear if sodium is present.

#### Potassium ( $\text{K}^+$ ).

Add a drop of chloroplatinic acid near the drop to be tested (only a portion of the original sample should be used) and then draw the two drops together. High refractive isotropic orange octahedra indicate the presence of potassium. Ammonium forms isomorphous crystals with chloroplatinic acid and must be tested for by the method described below. If the ammonium test is negative, then the presence of potassium is confirmed.

#### Ammonium ( $\text{NH}_4^+$ ).

A hanging drop method is used to test for the ammonium ion. Take a drop of the chloroplatinic acid and place it in the center of a coverslip. Take the sample to be tested and place it on a microscope slide and encircle it with a piece of glass tubing (8 mm length, 12 mm I.D.). Add a little dilute NaOH to the substance on the microscope slide and cover the glass ring immediately with coverslip (inverted) bearing the chloroplatinic acid. Yellow octahedra will appear in the hanging drop of chloroplatinic acid which confirms the presence of ammonium. Slight warming of the slide may speed the migration of the ammonia to the reagent drop.

#### Lead ( $\text{Pb}^{++}$ ).

Add a very tiny crystal of potassium iodide to a drop of water on a microscope near the very dilute test drop and draw the two drops together with the drawn-out glass tip. Bright yellow hexagonal plates will form often showing thin-film interference colors. Excess KI will convert these hexagons to white needles.

#### Barium ( $\text{Ba}^{++}$ ).

A drop of saturated aqueous squaric acid is placed on a microscope slide near the test drop (acidified with nitric acid). When the drops are allowed to run together, barium forms blades and parallelopipeds (singly and in rosettes).

#### Nitrate ( $\text{NO}_3^-$ ).

Test No. 1: Dissolve a crystal of nitron in a drop of dilute acetic acid on a microscope slide near a drop of unknown substance. Draw the drops together and at once you will obtain

sheaves of long, very slender needles and imperfect radiates.

Test No. 2: Dissolve a crystal of sulfanilic acid and a crystal of alpha-naphthylamine in a drop of dilute acetic acid on a microscope slide (or white spot plate). Add the test substance and a minute amount of zinc dust. A deep red color is produced.

#### Chlorate ( $\text{ClO}_3^-$ ).

Place a drop of distilled water on a microscope slide (or white spot plate) and acidify with  $\text{H}_2\text{SO}_4$ . Add a crystal of aniline sulfate and then the substance to be tested. A greenish-yellow is produced which goes to blue color. Also, an odor of chlorine gas can usually be detected. This test is not considered specific for chlorates.

#### Perchlorate ( $\text{ClO}_4^-$ ).

The substance to be tested is dissolved in a drop of water and a few crystals of strychnine sulfate is added. A precipitate of simple rectangular and lath crystals will develop.

### APPENDIX II

#### Barium Nitrate

Crystal Class: Cubic  
Refractive Index:  $n = 1.571$   
Melting Point:  $592^\circ$

#### Potassium Nitrate

Crystal Class: Orthorhombic  
Refractive Indices:  $\alpha = 1.335$ ,  $\beta = 1.5056$ ,  $\gamma = 1.5064$   
Birefringence: 0.1714  
 $2V = 7^\circ (-)$   
Fusion Data: Inverts at  $129^\circ\text{C}$  to rhombohedral phase.  
Melting Point:  $333^\circ$

#### Ammonium Nitrate

Crystal Class: Orthorhombic at  $25^\circ\text{C}$   
Refractive Indices:  $\alpha = 1.413$ ,  $\beta = 1.611$ ,  $\gamma = 1.637$   
Birefringence: 0.224  
 $2V = 35^\circ (-)$   
Fusion Data: Converts to biaxial form at  $32^\circ\text{C}$ , to tetragonal form at  $84^\circ\text{C}$ , and to cubic form at  $125^\circ\text{C}$ .  
Melting Point:  $155^\circ\text{C}$ .

#### Sodium Nitrate

Crystal Class: Hexagonal  
Refractive Indices:  $\omega = 1.5874$ ,  $\epsilon = 1.3361$   
Birefringence: 0.2493  $(-)$   
Melting Point:  $308^\circ\text{C}$

#### Lead Nitrate

Crystal Class: Cubic  
Refractive Index:  $n = 1.781$   
Melting Point:  $470^\circ$

#### Ammonium Perchlorate

Crystal System: Orthorhombic  
Refractive Indices:  $\alpha = 1.4818$ ,  $\beta = 1.4833$ ,  $\gamma = 1.4881$   
Birefringence: 0.0063  
 $2V = 70^\circ (-)$   
Melting Point: Decomposes on heating

#### Potassium Perchlorate

Crystal System: Orthorhombic  
Refractive Indices:  $\alpha = 1.4731$ ,  $\beta = 1.4737$ ,  $\gamma = 1.4769$   
Birefringence: 0.0038  
 $2V = 50^\circ (+)$   
Melting Point: Decomposes at  $400^\circ\text{C}$

#### Sodium Perchlorate

Crystal System: Orthorhombic

Refractive Indices:  $\alpha = 1.4606$ ,  $\beta = 1.4617$ ,  $\gamma = 1.4730$

Birefringence: 0.0124

Melting Point: Decomposes on heating

Note: May also exist as hydrate form which belongs to monoclinic crystal class.

#### Potassium Chlorate

Crystal System: Monoclinic

Refractive Indices:  $\alpha = 1.415$ ,  $\beta = 1.517$ ,  $\gamma = 1.523$

Birefringence: 0.108

2V = 28° (-)

Melting Point: 368°

#### Sodium Chlorate

Crystal Class: Cubic

Refractive Index:  $n = 1.518$

Melting Point: 248°

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## ION CHROMATOGRAPH OF EXPLOSIVES AND EXPLOSIVE RESIDUES

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**ABSTRACT.** Explosives which contain primarily water soluble ingredients are frequently encountered by the forensic scientist. Determining the identity of the many slurry explosives now being used in a growing number of bombing cases is one area where ion chromatography (IC) has been most useful. There are numerous commercial dynamites and blasting agents sold by approximately a dozen major manufacturers which are all comprised primarily of  $\text{NH}_4\text{NO}_3$ ,  $\text{KNO}_3$  and  $\text{NaNO}_3$ , with varying amounts of water and both ionic and non-ionic additives. If the wrapper has been removed from these products before they are incorporated into an improvised explosive device (IED), their identification can be a formidable task. With the voluntary cooperation of explosive manufacturers, the FBI Laboratory is building a collection of commercial products most likely to be used in IED's. In order to analyze these explosives, the Laboratory has developed novel procedures for sample preparation and has developed IC procedures for some ions which were not previously determined by IC. The extremely high sensitivity and selectivity of IC makes the technique extremely valuable for the analysis of post-blast residues. Following extraction of the debris with water or a water-methanol solution, the extract is simply filtered and run on the IC under conditions identical to those used for the analysis of the undetonated explosive. We have shown that this form of analysis offers several advantages over other techniques when the ionic residues are volatile or electrochemically active.

Since its introduction to the FBI Laboratory in early 1980, Ion Chromatography (IC) has been used to determine ionic materials in many cases. One of the most successful applications of IC has been in the analysis of explosives.

Ion Chromatography is a new term for most people in the field of explosives analysis. Despite several excellent review articles on IC (1, 2, 3) it is appropriate to give an elementary introduction to the subject before describing the specialized applications which we have developed. IC is a sub-discipline of high pressure liquid chromatography (HPLC) which is applicable to the determination of all ionic material. The instrument itself is essentially an HPLC which uses an analytical column packed with a low capacity ion exchange resin. The mobile phase (also called eluent) is an aqueous buffer solution which may contain some

organic solvent such as methanol or acetonitrile. In the chromatographic process, the ions are partitioned between the ion exchange resin and the eluent. Those ions with low  $\text{pK}_a$ 's are generally retained least, although ionic size and overall charge can also influence retention. The eluent strength is determined by the  $\text{pK}_a$  of the salt (s) used to make the buffer solution and by the ionic strength of the solution. Selectivity is influenced by the pH and dielectric constant of the eluent.

Detection can be accomplished by an HPLC detector which responds to the ions of interest. Conductivity detection is most commonly used because, by definition, it responds to all ions in aqueous solutions. Modern technology allows flow-through conductivity cells with advantages of simplicity, sensitivity, reproducibility and linearity. The major problem associated with con-



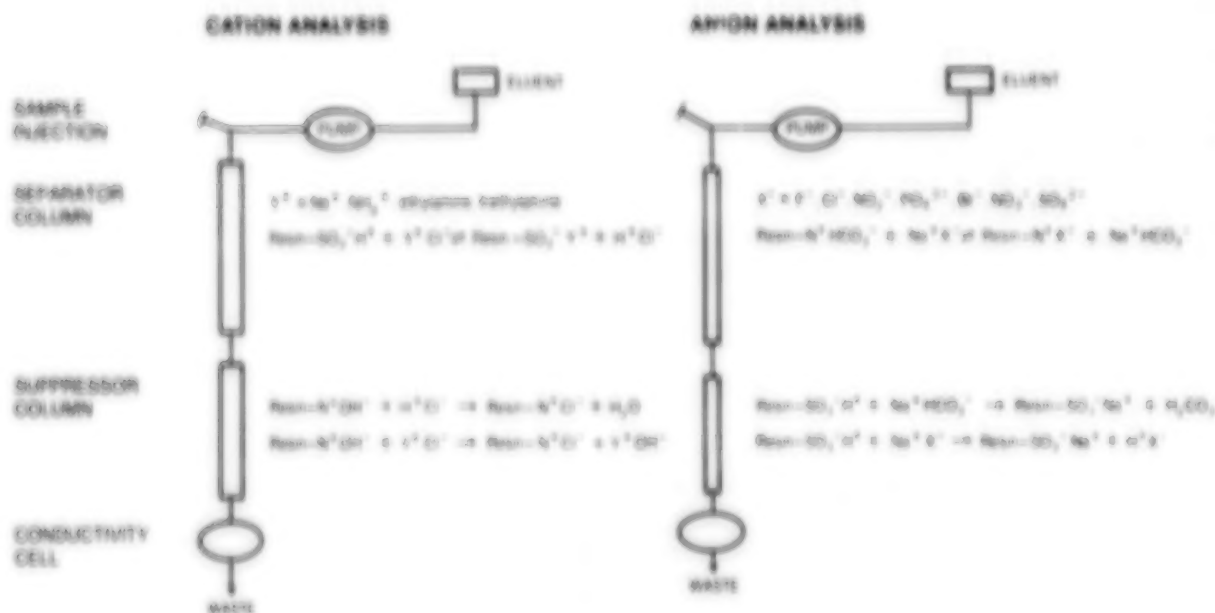


Figure 1.

ductivity detection is that it responds to both sample ions and ions in the buffer solution. Reasonable analysis times require eluents of approximately 0.01M buffer salt. This is much more concentrated than the ppm sample ion concentrations which most analysts are interested in determining.

There are two different instrumental approaches to overcome the buffer conductivity problem. The most popular uses an additional, high capacity ion exchange column to remove the highly conductive buffer ions before the eluent reaches the conductivity detector. Figure 1 illustrates how this works for the analysis of anions. This technology was invented by Small, Brown, and Stevens (1972), then patented and published in 1975. The FBI uses instruments of this type. The alternative instrumental approach to the buffer/conductivity problem does not employ a second column. This technique is explained in another paper in this symposium by Dominic Barstott.

The utility of IC for the analysis of explosives is obvious when one considers the ingredients used in commercial or homemade pyrotechnics, and slurry explosives. Perchlorate and nitrate salts are the most commonly used oxidizers in domestically produced commercial pyrotechnics and homemade formulations (see Figure 2). Figure 3 shows some ingredients used in "water-based" explosives. Ammonium nitrate is the major ionic ingredient in these gels. Other salts such as  $NaNO_3$ ,  $KNO_3$ , and  $Ca(NO_3)_2$  are used as oxidizers. For

slurry dynamites, alkylamine nitrates, alkylamine nitrates and perchlorate salts are often used as sensitizers.

Slurry explosives are manufactured by approximately a dozen companies in the United States. Each manufacturer offers several formulations, each intended for a particular purpose. Correctly identifying an unknown slurry by comparing analytical results to a library of formulations of known slurries is a formidable task. To be successful a chemist must have a complete and up-to-date collection of known explosives. Further, he

## COMMON INGREDIENTS FOUND IN PYROTECHNICS

### OXIDIZERS

$KClO_4$   
 $NH_4ClO_4$   
 $KNO_3$   
 $KClO_3$   
 $Ba(ClO_3)_2$   
 $Ba(NO_3)_2$   
 $Sr(NO_3)_2$

### FUELS

Al (powdered)  
 C (powdered)  
 PVC  
 Dextrin  
 Sucrose  
 Ti (powdered)  
 Red Gum  
 $Sb_2S_3$   
 Mg (powdered)  
 S (powdered)

Figure 2.



## SOME INGREDIENTS OF "WATER-BASED EXPLOSIVES"

Oxidizers	Fuels	Sensitizers
$\text{NH}_4\text{NO}_3$	Al (powdered)	Al (powdered)
$\text{NaNO}_3$	Wood Pulp	$\text{CH}_3\text{CH}_2\text{ONH}_2 \pm \text{NO}_2$
$\text{KNO}_3$	Charcoal	$\text{CH}_3 - \text{NH}_2 \pm \text{NO}_2$
$\text{Ca}(\text{NO}_3)_2$	Coal	Fuel Oil
Air	Fuel Oil	(Picric Acid)
		(Ammonium Picrate)

Figure 3.

must be capable of both qualitative and quantitative analysis for the ingredients in each formulation.

In a forensic laboratory, where one individual may be responsible for analyzing all the ingredients in a sample, IC offers significant advantages when compared to some alternative methods. All ionic materials can, at least in principle, be determined by IC. An individual using one instrument can do a complete analysis of all ionic material in a sample. The sample preparation for analysis of explosives by IC is shown in Figure 4. This procedure, which involves only homogenizing, filtering, and diluting is very quick. Sample preparation for other types of analysis involve lengthy, time consuming steps such as digestion, extraction, precipitation, heating, drying, volatilization or derivatization. By eliminating such procedures, the problems of altering the sample through oxidation, reduction, volatilization, incomplete reactions or poor extractions are completely eliminating. The major source of quantitative error for determining ionic ingredient in explosives by this IC procedure is in obtaining a representative sample.

### STEPS IN IC ANALYSIS OF "WATER-BASED EXPLOSIVES" AND PYROTECHNICS

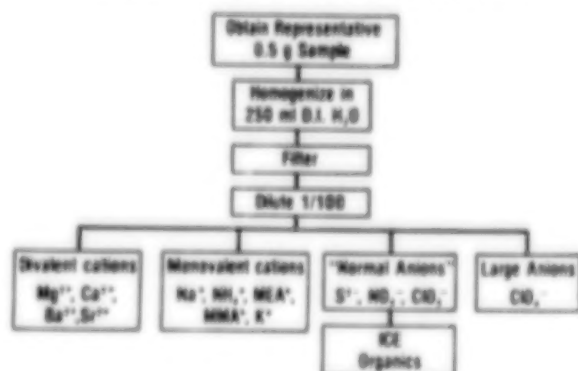


Figure 4.

The ion chromatographs in the FBI Laboratory are routinely run with more than one detector in line (see Figure 5). Whenever possible at least two of the detectors are used simultaneously for a single chromatographic run. The responses are ratioed and these ratios are compared with the results from standards. This practice helps assure both the qualitative and quantitative accuracy of the results. When sufficient sample is available, independent spectroscopic methods are used to verify the components in the composition.

Most of the IC procedures for determining the anions in explosives are borrowed from other applications and used with little or no modification. Nitrate can be determined along with F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup> in a single run using a Na<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>HCO<sub>3</sub> eluent. Both conductivity and ultraviolet (UV) absorbance detectors are used in series. The UV detector selectively responds to NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> at 210nm. This procedure is modified somewhat by a selective reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> before IC analysis to allow for the determination of small amounts of ClO<sub>3</sub><sup>-</sup> in the presence of NO<sub>3</sub><sup>-</sup> (see Figure 6). Perchlorate is determined in a separate IC run using an eluent of 0.005 M NaI and a silver form halide suppressor column. No anions have been found to interfere with ClO<sub>4</sub><sup>-</sup>, and this method offers ppm sensitivity (4).

Methods suitable for the analysis of the monovalent cations in explosives had to be developed when the published IC procedures proved inadequate for explosives analysis (5). Many monovalent alkylamines and alkolamines which are or can be used as sensitizers in slurries are unresolved from alkali metals using aqueous HCl or HNO<sub>3</sub> eluents. Figure 7 shows a chromatogram of a solution containing 10ppm each of Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and monomethylamine (MMA). There K<sup>+</sup> and

### SYSTEM FOR ANALYSIS OF ANIONS IN EXPLOSIVES AND EXPLOSIVE RESIDUES

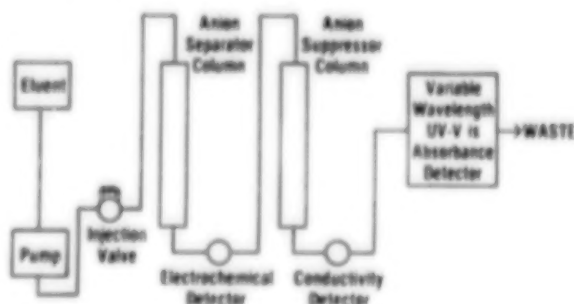


Figure 5.

# QUANTITATION OF 1 ppm $\text{ClO}_3^-$ IN 20 ppm $\text{NO}_3^-$

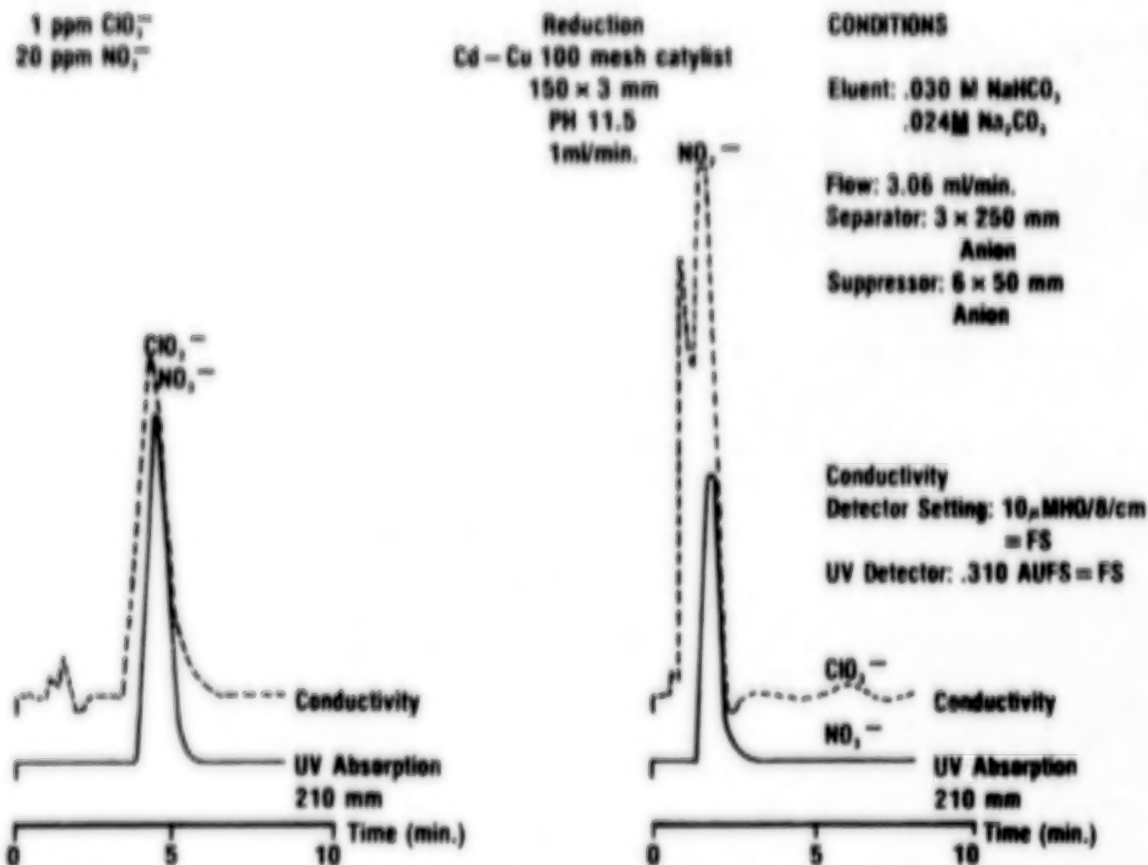


Figure 6.

MMA appear as one unresolved peak. The addition of 40 percent methanol to the eluent changes the column selectivity (6) and allows for baseline resolution of all four cations (Figure 8). Figure 9 shows the chromatogram of the monovalent cations in a DuPont Tovex dynamite. The column

selectivities for several alkylamines, alkolamines, and alkali metals were determined for eluents containing concentrations of methanol ranging from 0 to 40 percent (Figures 10 & 11).

## ANALYSIS OF MONOVALENT CATIONS IN "WATER-BASED EXPLOSIVES"

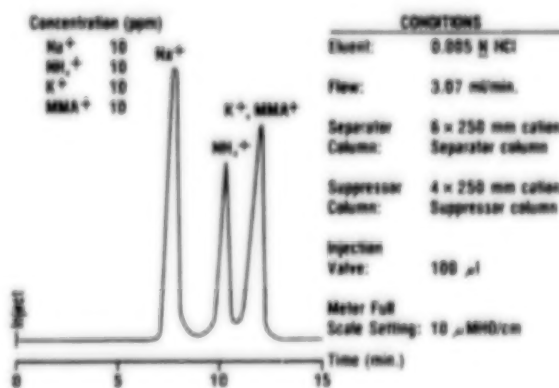


Figure 7.

## ANALYSIS OF MONOVALENT CATIONS IN "WATER-BASED EXPLOSIVES"

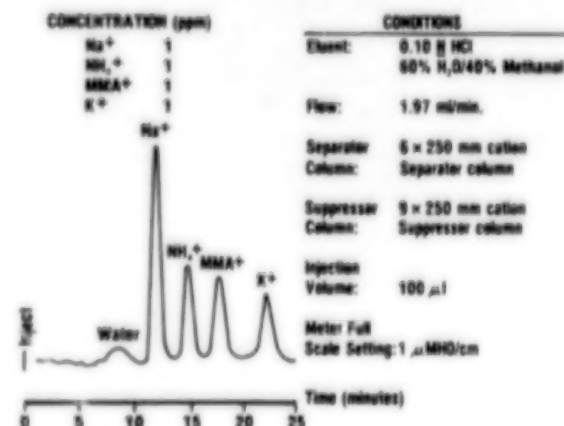


Figure 8.

# ANALYSIS OF MONOVALENT CATIONS IN A SAMPLE OF "TOVEX"

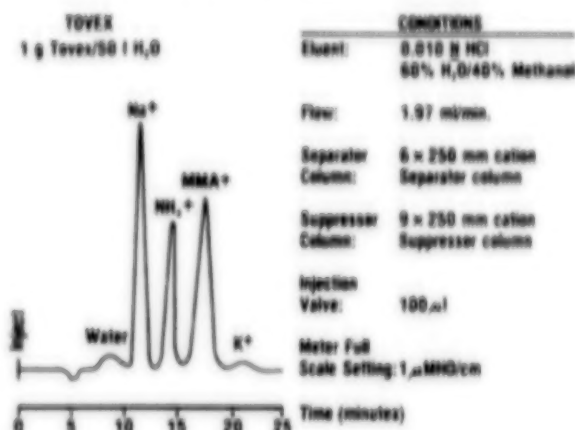


Figure 9.

The determination of divalent cations in slurries has become more important recently with the increasing use of  $\text{Ca}(\text{NO}_3)_2$  as a partial replacement for  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ , and  $\text{KNO}_3$ . Calcium ion can be determined along with  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  in a single IC run using a procedure developed for a general analysis of soluble alkali earths (Figure 12) (7). Diperchlorate or dinitrate salts of ethylene-diamine have also been used to sensitize slurry explosives. A suitable procedure for ethylene-diamine determination was developed (8) by this laboratory. That procedure has a minimum detectable limit of 0.5ppm and is linear between 0 and 25ppm. A representative chromatogram is shown in Figure 13.

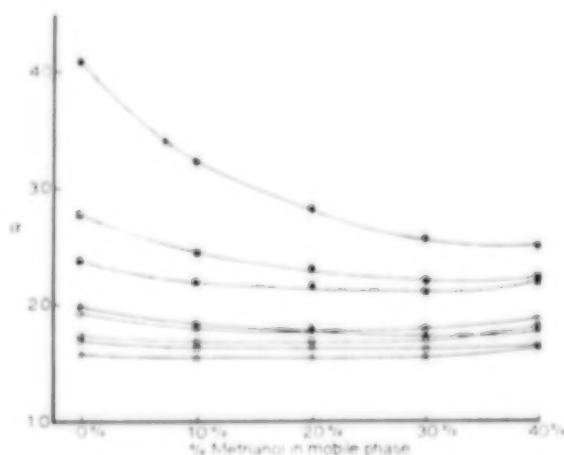


Figure 10. Relationship between selectivity ( $\alpha$ ) and percent methanol in the mobile phase for monoamine cations.  $\Delta$  = Ethanolamine,  $\square$  = diethanolamine,  $\circ$  = methylamine,  $\blacktriangle$  = triethanolamine,  $\diamond$  = ethylamine,  $\blacklozenge$  = triethylamine,  $\bullet$  = diethylamine,  $\blacksquare$  = trimethylamine.

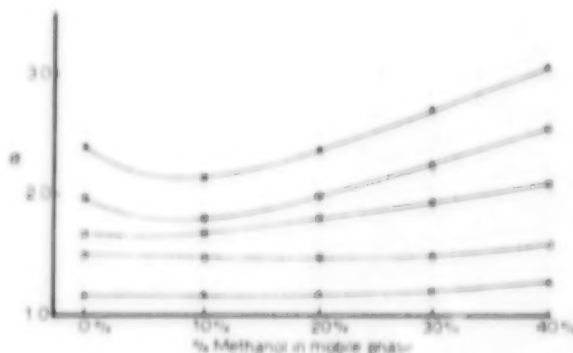


Figure 11. Relationship between selectivity ( $\alpha$ ) and percent methanol in the mobile phase for inorganic monovalent cations.  $\Delta$  =  $\text{Na}^+$ ,  $\circ$  =  $\text{NH}_4^+$ ,  $\square$  =  $\text{K}^+$ ,  $\diamond$  =  $\text{Rb}^+$ ,  $\blacktriangle$  =  $\text{Cs}^+$ .

The FBI Laboratory is constantly updating their files of commercial explosives. When a new formulation is introduced into the market, the laboratory will examine the explosive to determine if the available methods of analysis are adequate to distinguish it from other products. If not, a research project will be initiated to develop the needed methods.

## EXPLOSIVE RESIDUES

The primary differences between analyzing explosives and their post-blast residues are in sample preparation and data interpretation. The high sensitivity and non-destructive sample preparation offered by IC give it significant advantages over other analytical methods used to analyze residues.

Bomb fragments or debris from the point of explosion are extracted with cold deionized water. Large specimens can be rinsed using a wash bottle

# ANALYSIS OF DIVALENT CATIONS IN IREMIT

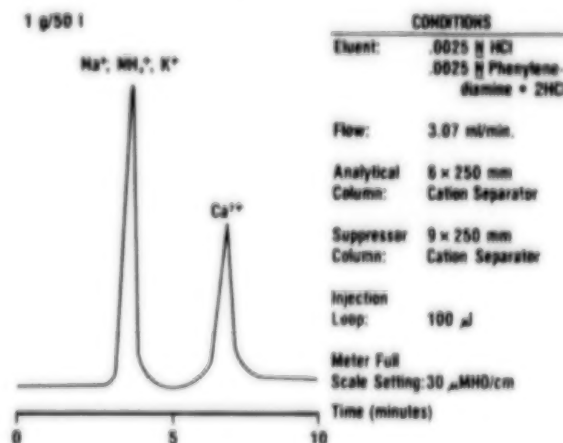


Figure 12.

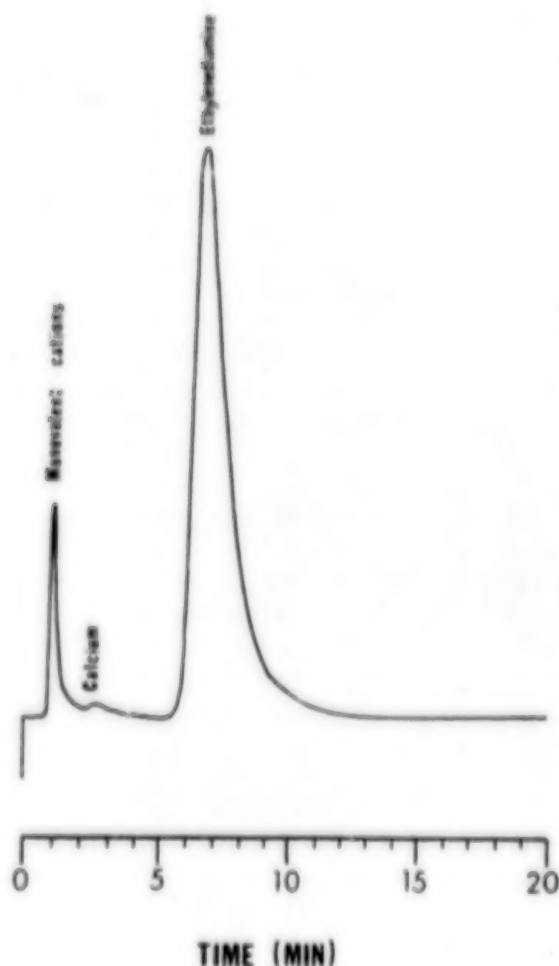


Figure 13.

and the extract collected in a plastic or stainless steel tray. A minimum volume of water should be used. If it is necessary to rinse the debris with more than 250ml of water, it is advantageous to re-use some of the water already collected in the tray to prevent diluting the extract. Smaller specimens are best extracted by placing them in a beaker and covering them with a minimal amount of water, followed by several minutes of an ultrasonic bath. Table I shows the solubilities of some salts which would be important to an investigation if identified in debris. Also listed are solubilities of some building materials which cause interference. Most oxidizers and ionic sensitizers are very soluble in cold water. The use of warm or hot water will most often increase the background levels due to increased solubility of interferences. Following extraction, the solution is filtered to remove insoluble particulates which could plug the valves or poison the column. The filtered extract is then injected onto the IC using the same chromatograph-

ic procedures outlined earlier for analysis of explosives.

Table I. SOLUBILITIES OF SOME SALTS USED IN EXPLOSIVES AND SOME COMMON INTERFERENCES

Salt	Solubility (g/100 ml)
Salts Used in Explosives	
NaNO <sub>3</sub>	73
NaClO <sub>3</sub>	79
NH <sub>4</sub> NO <sub>3</sub>	65
Ca(NO <sub>3</sub> ) <sub>2</sub>	129
MMA-NO <sub>3</sub>	>150
Common Interferences	
CaSO <sub>4</sub> •2H <sub>2</sub> O	0.24
CaCO <sub>3</sub>	0.0015
NaCl	35.7
CaHPO <sub>4</sub>	1

Once the sample has been extracted the solution is susceptible to deterioration. Concentrations of alkylamines, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> have all been shown to be significantly diminished in a solution even if refrigerated in a sealed teflon bottle. Presumably the ions are metabolized by bacteria or undergo electrochemical reactions with other ions in the solution.

## DISCUSSION

The interpretation of analytical results derived from the analysis of debris by IC can again be a complicated task. Generally, more ions are measured at a higher sensitivity with IC than with other methods. Consequently the examiner cannot rely on a database which was collected using other, less sensitive techniques to interpret the IC data. In all controlled tests conducted by the post-blast FBI, all ions found in the original explosive were detected in the residues, provided that the residues were extracted and analyzed within 24 hours after detonation. The relative concentration of ions changed predictably from the relative concentrations in the unconsumed explosive. Those materials with high vapor pressure and those which are thermally labile will be found in much lower concentrations than alkali metals or halides. Figure 14 shows the monovalent cations detected in a residue from a Tovex device. Comparing this chromatogram with that shown in Figure 9 illustrates the point. Another consideration is that explosions are short, high temperature events. Consequently, reaction products which would not be thermodynamically predicted under easily obtain-

able laboratory conditions can be formed. An example is the formation of  $\text{NO}_2^-$  in an explosion where no form of oxidized nitrogen was incorporated in the explosive. The  $\text{NO}_2^-$  was most probably formed from air according to the reaction:



The process can become even more complicated by the fact that  $\text{NO}_2^-$  is readily oxidized to  $\text{NO}_3^-$  by the dissolved oxygen in water. Thus it is not uncommon to measure trace  $\text{NO}_3^-$  in residues from  $\text{KClO}_3$ /Sugar devices. Another example is the formation of  $\text{NH}_4^+$  during the detonation of black powder.

#### MONOVALENT CATIONS IN THE RESIDUE OF A "WATER-BASED EXPLOSIVE"

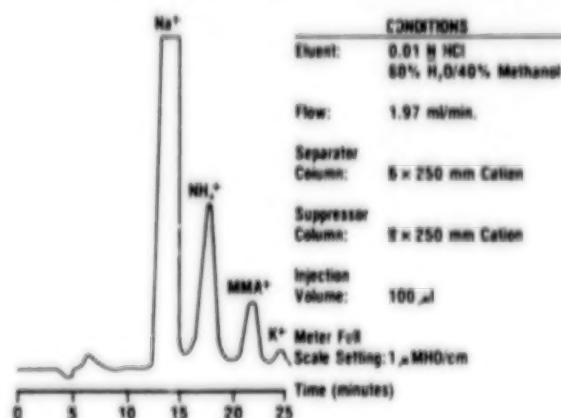


Figure 14.

When the FBI Laboratory first began to analyze explosive residues by IC, the chromatograms showed the presence of ionic material which could be relevant to the case, many of which were completely missed by X-ray powder diffraction (XRD) and chemical spot tests. An experiment was designed to compare the capabilities of XRD and IC in analyzing the ionic content of

bombing residues. Black powder pipe bombs,  $\text{KClO}_3$ /sugar pipebombs, and water based explosives were detonated in metal containers, or in crates approximately meter deep. Following detonation of each device, samples were collected and brought to the laboratory and analyzed within 24 hours following the schematic illustrated in Figure 15. The XRD results were not quantitated. The IC results for the same residues were quantitated before and after the residue was subjected to XRD analysis to show the effect of drying the residue to a powder. Table 2 shows this effect for a  $\text{KClO}_3$ /sugar pipe bomb residue. The first IC run clearly identifies  $\text{ClO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{K}^+$  along with

#### ESTABLISHED METHOD OF ANALYSIS FOR INORGANIC EXPLOSIVE RESIDUES

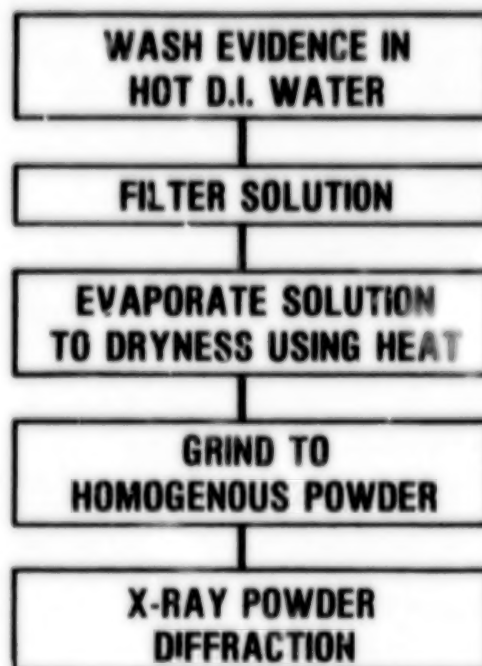


Figure 15.

Table 2. EFFECT OF DRYING  $\text{KClO}_3$ /SUGAR PIPEBOMB RESIDUE FOR ANALYSIS BY X-RAY POWDER DIFFRACTION

Ions	Original Wash by I.C. (wt%)	X-ray Powder Diffraction (Crystals Identified)	Reconstituted Powder by I.C. (wt%)
K <sup>+</sup>	41.6	KCl, KClO <sub>3</sub>	44.3
ClO <sub>3</sub> <sup>-</sup>	43.0	KClO <sub>3</sub>	28.7
Cl <sup>-</sup>	14.0	KCl	26.2
Na <sup>+</sup>	.4		.5



small amounts of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{Na}^+$ . The XRD is successful in qualitatively identifying  $\text{KClO}_3$  and  $\text{KCl}$  but did not detect any other materials. The analysis of the reconstituted powder by IC shows that nearly half of the  $\text{ClO}_3^-$  had been reduced to  $\text{Cl}^-$  during the sample preparation and XRD analysis. In this test the reduction of  $\text{ClO}_3^-$  did not prevent XRD from identifying  $\text{KClO}_3$  crystals in the residue. The IC has been used to analyze residues in real bombing cases where it detected minute quantities of  $\text{ClO}_3^-$  is important; when found in any concentration, because it has no natural sources. Furthermore,  $\text{ClO}_3^-$  will not be found in the absence of  $\text{ClO}_4^-$  if the latter were used as the oxidizer because  $\text{ClO}_4^-$  is more stable toward reduction than  $\text{ClO}_3^-$ . Since all commercial pyrotechnic devices produced domestically use  $\text{ClO}_4^-$ , it is safe to assume that when  $\text{ClO}_3^-$  is found in the absence of  $\text{ClO}_4^-$  that the device originated from foreign pyrotechnics or was a homemade formulation. Conversely,  $\text{ClO}_4^-$  is not formed as the result detonation of a  $\text{ClO}_3^-$  oxidized device, consequently the presence of  $\text{ClO}_4^-$  in residue is indicative of a device derived from a U.S. made commercial pyrotechnic.

The tests conducted with the detonation of water-based dynamites were even more dramatic in demonstrating how sample preparation can adversely affect the results of an analysis. Table 3 shows a typical result of debris recovered from a device made with Tovex dynamite. The first IC run was able to easily detect  $\text{Na}^+$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{MMA}^+$  and other ions. The analysis by XRD showed only  $\text{NaNO}_3$ . The second analysis by IC performed on the powder after it was redissolved in DI water shows one reason for the discrepancy; Ammonium Nitrate is highly volatile. It decomposes according to the reaction:  $\text{NH}_4\text{-NO}_{3(s)} \rightarrow \text{NH}_{3(g)} + \text{HNO}_{3(g)}$  with a  $K_{eq} = (20\text{ppb})^2$ . Mono-

methylamine nitrate is at least as volatile. Furthermore,  $\text{MMA-NO}_3$  is highly hyposcopic which opens the possibility that it may not have been in crystalline form at the time when the XRD analysis was performed. The volatility of the salts is demonstrated by the fact that 94% of the  $\text{NH}_4^+$  ion and 90% of the  $\text{MMA}^+$  ion were lost between the times of the first and second IC analysis. It is also interesting to note that most of the  $\text{NO}_2^-$  and  $\text{Cl}^-$  were lost as a result of XRD analysis. Presumably, the  $\text{NO}_2^-$  was oxidized to  $\text{NO}_3^-$ , while the  $\text{Cl}^-$  was lost by the volatilization of  $\text{NH}_4\text{Cl}$ .

If these debris has been from a bombing case, and the evidence had been properly collected, stored and promptly analyzed, the examiner may have been able to correctly identify Tovex as the explosive in this case to the exclusion of all other domestically manufactured dynamites if he had used IC. On the other hand, if that same evidence were to have been analyzed by XRD, the examiner would only have been able to state that the oxidizer was most probably  $\text{NaNO}_3$  which is common in most water-based dynamites, blasting agents and can be easily purchased in pure form for the manufacturer of an improvised explosive formulation.

## CONCLUSION

The FBI Laboratory has demonstrated that IC can be an important tool for the analysis of pyrotechnics, dynamites, blasting agents and their post detonation residues. The techniques have proven to be adaptable to the determination of all ionic materials currently used in water-based explosive and most ionic materials in commercial pyrotechnics. The results obtained by this technique have proven to both quantitatively and qualitatively reliable when performed by scientists who are

Table 3. EFFECT OF DRYING "WATER-BASED EXPLOSIVE" RESIDUE FOR ANALYSIS BY X-RAY POWDER DIFFRACTION

Ions	Original Wash by I.C. (wt%)	X-ray Powder Diffraction (Crystals Identified)	Reconstituted Powder by I.C. (wt%)
$\text{Na}^+$	50	$\text{NaNO}_3$	64
$\text{NO}_3^-$	40	$\text{NaNO}_3$	34.2
$\text{NH}_4^+$	1.7		.1
$\text{MMA}^+$	1.0		.1
$\text{K}^+$	.25		.25
$\text{NO}_2^-$	1.0		.15
$\text{Cl}^-$	4.0		.3
$\text{SO}_4^{2-}$	0.1		.5



knowledgeable in the fundamental process underlying ion exchange chromatography and ion detection. Finally, the IC will probably continue to be used by the FBI Laboratory to aid in the analysis of ionic materials for the foreseeable future.

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# THE USE OF ION CHROMATOGRAPHY IN THE ANALYSIS OF WATER GEL EXPLOSIVES

D. J. Barsotti, R. M. Hoffman, and R. F. Wenger

**ABSTRACT.** This method involves the use of 10%  $\text{HNO}_3$  to break down the crosslinked network of the water gel. The resulting solution is filtered to remove the insoluble components, i.e. glass, perlite, hydrolyzed quar and organic fuel. The filtrate is diluted to decrease the individual in concentrations to approximately 100 ppm. Two sets of chromatographic conditions are necessary for a complete analysis, one set for the monovalent cations  $\text{Na}^+$ ,  $\text{CH}_3\text{NH}_3^+$ ,  $\text{NH}_4\text{NH}_4^+$ , etc. and another for the multivalents such as calcium, etc. Using dual column dual conductivity detector ion chromatography the concentration is determined using a previously determined response factor for each ion of interest. The described method will reduce the analysis time from several hours to thirty minutes. The precision (2 $\sigma$ ) is 5% relative.

## INTRODUCTION

The use of liquid chromatography has been extended to the analysis of water gel explosives. Traditional standard methods are both tedious and time consuming. These methods are based on solubility differences of individual components and the reactions of various components with a given reagent to form an insoluble precipitate or a volatile substance.

These standard methods have been used for the past twenty years and although these methods can be accurate and reproducible, the analyses are time consuming taking approximately 3–5 hours. As such, these methods are inappropriate for process control when the analyses are for manufacturing processes. Therefore, a method was needed which is more sensitive and rapid to meet requirements for in process control, quality assurance and troubleshooting. The desired analyses time is approximately 30 minutes.

In recent years many techniques have been proposed in literature using chromatography for the analyses of explosives. Some of these techniques include gas liquid chromatography (1, 2), thin layer chromatography (3, 4), and liquid chromatography (5). The technique of ion chromatography was developed by Small, *et al.* (6) in 1975. This technique called suppressor-type ion chromatography uses the combination of an analytical separating column in conjunction with a suppressor column which is used to remove background elements in the eluent. A variation to this tech-

nique was proposed by Fritz, *et al.* (7). This system uses a conventional HPLC equipment with separating column and a conductivity detector. This system (nonsuppressed IC) is readily adopted to most liquid chromatographs.

The nonsuppressed system was used to determine the inorganic salts,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{CH}_3\text{NH}_3^+$ , and  $\text{Ca}^{++}$ . This represents approximately 80% of the "Tovex" explosives. This analysis time is reduced to 25 minutes with a precision of 5% relative.

## EXPERIMENTAL

### Apparatus

Ion Chromatograph (IC)—Wescan Model 261 with dual column and dual detector capability equipped with two fixed volume, high pressure injection valves and 100 sample loops.

Cation columns—Wescan Cat. No. 269-004, 25 cm x 2.0 mm I.D. with cation guard cartridges, Cat. No. 269-005.

The use of plasticware in place of glassware is recommended to prevent sodium contamination from the glass.

### Reagents

All reagents were ACS reagent grade and were without further purification except as noted.

Treated Water—Type I water or distilled water passed through a filter train consisting of a combination deionization/organic removal cartridge (Fisher Scientific, Cat. No. 09-035-30), and

Ultrapure cartridge (Fisher Scientific, Cat. No. 09-035-25), and a pleated capsule filter 0.2  $\mu$ m pore size (Fisher Scientific, Cat. No. 09-743-50). This water is used in all solution preparations:

Monomethylamine Nitrate (MMAN)—73%. Nitric Acid—"Ultrex" grade reagent, J. T. Baker, Cat. No. 4801, or equivalently pure nitric acid. The trace impurities in lower grades of Nitric Acid will contaminate the column causing unstable peak retention times.

### Column Rinsing Solutions

0.2M  $\text{HNO}_3$ —Dilute 1.25 ml Ultrex  $\text{HNO}_3$  to 100 ml with water. Transfer to a plastic sample bottle and tightly cap.

## RESULTS AND DISCUSSIONS

### Calibration

Prepare a stock solution by weighing 0.250 g  $\text{NaNO}_3$ , 0.500 g  $\text{NH}_4\text{NO}_3$ , 2.00 g  $\text{Ca}(\text{NO}_3)_2$ , and 0.480 g monomethylamine nitrate into a 100 ml plastic volumetric flask. Dissolve in 50 ml of treated water and dilute to the mark with treated water. Add 10 ml of stock solution to a 1000 ml plastic volumetric flask and dilute to the mark with treated water. Transfer this calibration solution to a plastic sample bottle and tightly cap. The concentration of  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{Ca}(\text{NO}_3)_2$  can be calculated from equation (1) and the concentration of monomethylamine nitrate can be calculated from equation (2).

$$\text{Conc; (ppm)} = (\text{g weighed;}) (100) \quad (1)$$

$$\text{Conc. MMAN(ppm)} = (\text{g weighed MMAN}) (73) \quad (2)$$

### Monovalent Cations

In the monovalent cation analysis ( $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , MMAN), stabilize one of the IC columns and detectors with these conditions: Mobile Phase - 0.0039 M  $\text{HNO}_3$  (0.250 ml Ultrex  $\text{HNO}_3$  /liter); Flow Rate - 1.8 ml/min; Detector - Range 10.

The columns are conditioned in the following manner; inject the 0.2 M EDTA solution and wait for signal to return to baseline, then inject 0.2 M  $\text{HNO}_3$  solution three times waiting for signal to return to baseline between injections.

Inject the calibration solution several times with an injection of 0.2 M  $\text{HNO}_3$  between calibration solution injections. Measure the peak area for  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , and MMAN and calculate a response factor (RF) for each compound:

$$\text{RF}_i = \frac{(\text{Conc; ppm})}{\text{Peak Area}_i}$$

Calculate the average RF for each component and use that for the sample analysis. The RF's and peak retention times should be determined daily.

### Divalent Ions

For the calcium analysis, stabilize the other IC column and detector with these conditions: Mobile Phase,  $1 \times 10^{-3}$  M ethylene diamine, pH adjusted to 6.1 with ultrex  $\text{HNO}_3$ ; Flow Rate, 1.5 ml/min; Detector, Range 10.

The columns are conditioned by injecting the 0.2 M EDTA solution three times, waiting for the signal to return to baseline between injections.

Inject the calibration solution several times, measure the peak area, and calculate a response factor (RF) for calcium.

$$\text{RF}_{\text{Ca}(\text{NO}_3)_2} = \frac{\text{Conc. Ca}(\text{NO}_3)_2 \text{ ppm}}{\text{Peak Area}_{\text{Ca}(\text{NO}_3)_2}}$$

Calculate the average RF and use it for the sample analysis. The RF's and peak retention times should be determined daily.

### Sample Analysis

Weigh 10 grams of explosives in a 250 ml volumetric flask. To break down the cross-linked network add 25 ml of 10% nitric acid. The hydrolysis time for most "Tovex" products is approximately 5 minutes. On formulas which contain higher levels of aluminum more nitric acid is needed along with a longer hydrolysis time. Other acids, such as,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  may be used, however, caution must be used when  $\text{HCl}$  is used in contact with stainless steel. The digested sample is diluted to 250 ml with treated water.

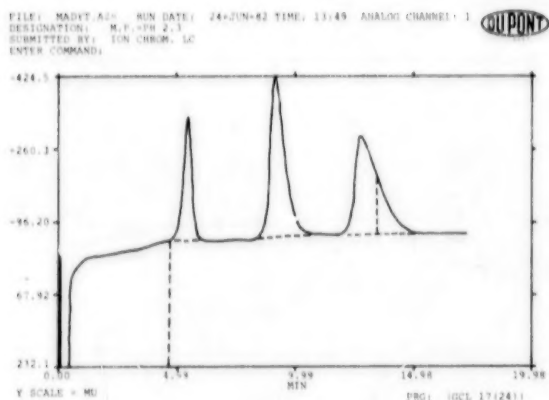
For the analysis of monovalent cations pipette 0.350 ml of sample solution into 100 ml plastic volumetric flask and dilute to mark with treated water. Running under monovalent cations conditions inject 100  $\mu$ l of sample and obtain peak areas and retention times for  $\text{Na}^+$ ,  $\text{NH}_4^+$ , and  $\text{CH}_3\text{NH}_3^+$ . Figure 1 is a typical scan of monovalent cation under the above conditions.

For the analysis of calcium pipette 3.5 ml of the sample solution into a 100 ml plastic volumetric flask and add 30 ml of 0.25 M  $\text{NaOH}$  and dilute to mark with treated water. The pH of this solution should be between 7-8. Running under divalent cation conditions inject 100  $\mu$ l of sample and obtain peak area for calcium.

### Calculations

For the monovalent cation analysis:

$$\% i = \frac{(\text{Peak Area}_i)(\text{RF}_i)(7.14)}{(\text{Sample Weight})}$$



For the calcium analysis:

$$\% \text{Ca(NO}_3)_2 = \frac{(\text{Peak Area})(\text{RF})(0.74)}{(\text{Sample Weight})}$$

Results for various "Tovex" analysis are shown in

Table 1. This list illustrates the comparison of results of present technique with those acquired using standard methods. Table 1 also indicates the precision of the various ions.

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Table 1. ION CHROMATOGRAPHIC ANALYSIS RESULTS FOR WATER GEL SAMPLES

		% MMAN			% AN			% CN			% SN		
Sample Number	"Tovex" Grade	Expected	Observed	Std. Dev.	Expected	Observed	Std. Dev.	Expected	Observed	Std. Dev.	Expected	Observed	Std. Dev.
1	300	36.72	36.12	0.66 <sup>(a)</sup>	30.82	29.83	0.79 <sup>(a)</sup>	—	—	—	13.96	13.57	0.25 <sup>(a)</sup>
2	800	19.99	20.99	0.042	42.94	41.68	1.29	—	—	—	8.57	8.13	0.21
					14.80	16.63	0.33	17.55	16.30	0.42	9.76	9.95	0.11
3	SSS	35.25	36.87	1.63	18.04	19.37	0.36	18.13	17.99	0.24	6.72	6.80	0.25
4	TR-2	30.03	30.96	2.00	23.47	23.99	1.01 <sup>(a)</sup>	—	—	—	13.21	13.44	0.20 <sup>(a)</sup>
5	Extra	17.28	19.49	0.90 <sup>(a)</sup>									

MMAN = Monomethylamine nitrate  
 AN = Ammonium nitrate  
 CN = Calcium nitrate  
 SN = Sodium nitrate

The expected values were obtained from the standard analysis.

The standard deviations (Std. Dev.) were calculated from 3 repeat runs, unless otherwise noted, and reported in absolute percent.

(a) The standard deviation was calculated from 5 repeat runs.

## Table 1. CONCLUSION

Ion chromatography can be the basis for a method to control process and quality in the manufacturing of water gel explosives. This method is rapid, reproducible and accurate.





## THE CHARACTERIZATION OF SOME LOW EXPLOSIVE RESIDUES BY ION CHROMATOGRAPHY

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**ABSTRACT.** A large percentage of improvised explosive devices encountered in bombing matters received by the FBI Laboratory involved the use of low explosives such as black powder, potassium chlorate/sugar mixtures and the commercial black powder substitute, Pyrodex. The combustion residues of most of these low explosives are inorganic in nature and water soluble. Because of this water solubility they can be analyzed both qualitatively and quantitatively by IC. The characterization of several different low explosives by IC is reported. This analysis provides a simple and rapid identification for these residues.

One of the latest analytical techniques to be applied to explosive analysis is ion chromatography (IC). Ion Chromatography is a term coined by the Dionex Corporation to encompass all techniques used for separating and quantitating both inorganic and organic ions and in its broadest sense is the chromatography of ions.

The FBI Laboratory has been using IC for two years in the analysis of explosives in bombing matters. Since its very limited use several years ago, the FBI Laboratory has greatly increased the use of IC until now it is routinely used in many bombing cases.

Because of its increased use in both high and low explosive bombing matters, but most especially in low explosive cases, it was decided to formulate a program of study to determine the extent and capability of IC in this type of analysis. The initial focus of the study was on low explosives.

It was the object of this study to characterize by IC, the pattern of anions and cations of the combustion products or residues of several different low explosives. It was felt if each different low explosive had its own individual IC anion and cation pattern or fingerprint, that IC could be used for a simple and rapid determination of the low explosives commonly used in improvised explosive devices (IED's).

Some of the initial goals were as follows:

1. Determine if a difference could be seen between homemade and commercial made black powder.
2. Determine if any ammonium salts were

formed in black powder residues.

3. Determine the level of sulfide and thiocyanate formed in black powder residues.
4. Determine the anion and cation pattern for each low explosive residue examined.

### EXPERIMENTAL AND INSTRUMENTATION

In the initial experiment four different low explosives were used, commercial black powder, homemade black powder, Pyrodex, a commercial black powder substitute and a 50/50 mixture of potassium chlorate and sugar.

The commercial and homemade black powders, were composed of potassium nitrate (75%), sulfur (10%) and charcoal (15%) while the Pyrodex is composed of potassium perchlorate, potassium nitrate, sulfur and charcoal.

Four different tests were conducted in which each of the four low explosive mixtures were placed in six-inch steel pipes capped at both ends and then exploded. The post-blast pipe fragments were collected and then washed with approximately 50ml. of distilled water. A 1 ml. sample of this filtered wash was then diluted 1/100 in distilled water. This sample was then analyzed by IC.

The analysis was performed on a Dionex Model 16 Ion Chromatograph equipped with a 100µl. sample loop and a 6µl. flow through conductivity detector. Two other detectors were also used in the test, a Dionex Electrochemical Detector with a 2.6µl. cell and Perkin-Elmer LC-35 variable wavelength UV-VISIBLE spectrophotometer with a 10µl. cell.



Figure 1. Block Diagram of Ion Chromatography Set-Up.

The anion separation was performed with Dionex columns i.e. a 3 x 50mm pre-column and a 4.0 x 250mm separator column in series with a Dionex anion fiber suppressor. The mobile phase for the anion analysis was 0.003 M  $\text{NaHCO}_3$ /0.0024M  $\text{Na}_2\text{CO}_3$  at a flow of approximately 3.0ml./min.

Cation separation was also performed on Dionex cation columns i.e. 3 x 50mm pre-column and a 6 x 200mm separator column in series with a 9 x 150mm. Dionex cation suppressor column. The mobile phase was 0.01N HCl in 30% ethanol.

Figure 1 is a block diagram of the IC instrumentation used in this test.

## RESULTS

Figure 2 is an ion chromatogram showing the separation of some of the common anions one

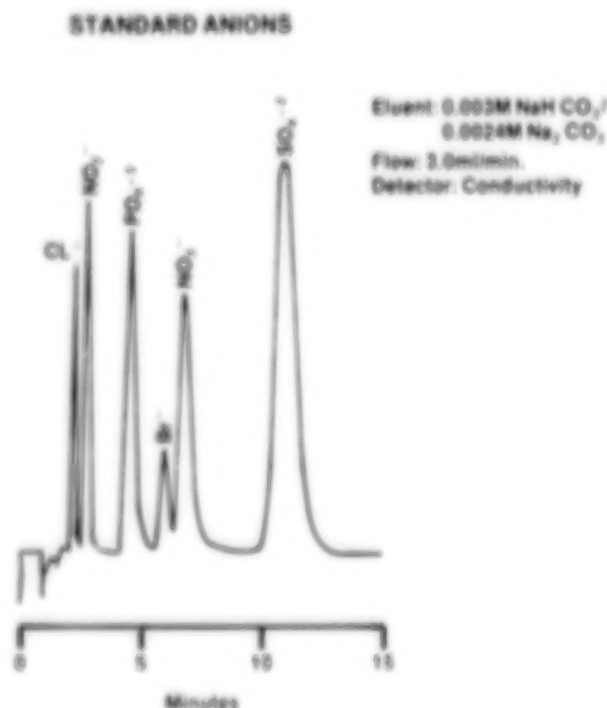


Figure 2. Separation of Common Anions. Peaks:  $\text{Cl}^-$ , 4ppm;  $\text{NO}_2^-$ , 10 ppm;  $\text{HPO}_4^{2-}$ , 50 ppm;  $\text{Br}^-$ , 10ppm;  $\text{NO}_3^-$ , 30ppm;  $\text{SO}_4^{2-}$ , 50ppm.

could experience in bombing matters. The retention time: shown in Figure 2 for the various anions were used as a basis of identification for the low explosive residue anion patterns.

Figures 3, 4, 5 and 6 shows the anion patterns for the residues of the four explosives used in the test. Homemade black powder (Figure 3) shows a large quantity of sulfate and a lesser quantity of nitrate from unreacted potassium nitrate. There also was a slight trace of nitrite ion present. Commercial black powder (Figure 4) has a very similar anion pattern to the homemade black powder. There is less nitrate in the residue and only a small trace of nitrite. This is probably due to the fact that commercial black powder usually burns more thoroughly and completely than homemade. In comparison of several different tests, however, it was too difficult to distinguish between homemade and commercial powders from their anion patterns alone.

Figure 5 shows the anion pattern of Pyrodex's combustion residue. The most prominent feature is the presence of chloride in the residue. Chloride

## HOMEMADE BLACK POWDER RESIDUE

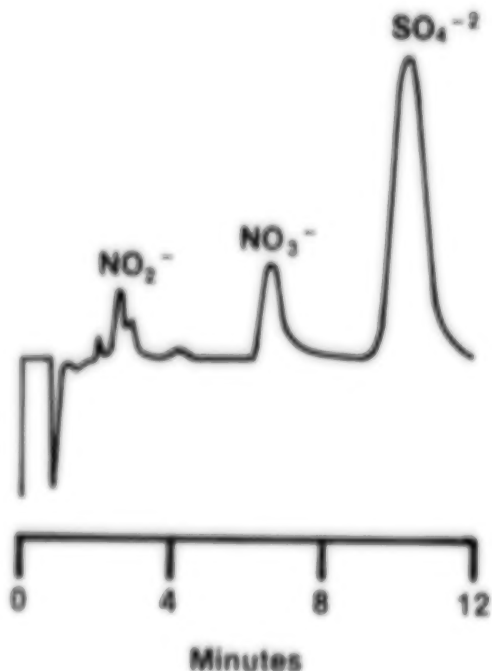


Figure 3. IC Anion Pattern for Home made Black Powder Combustion Residue.

# **COMMERCIAL BLACK POWDER RESIDUE**

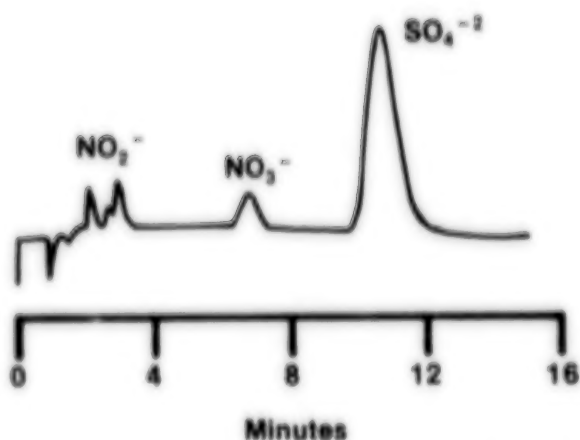


Figure 4. IC Anion Pattern for Commercial Black Powder Combustion Residue.

# **PYRODEX RESIDUE**

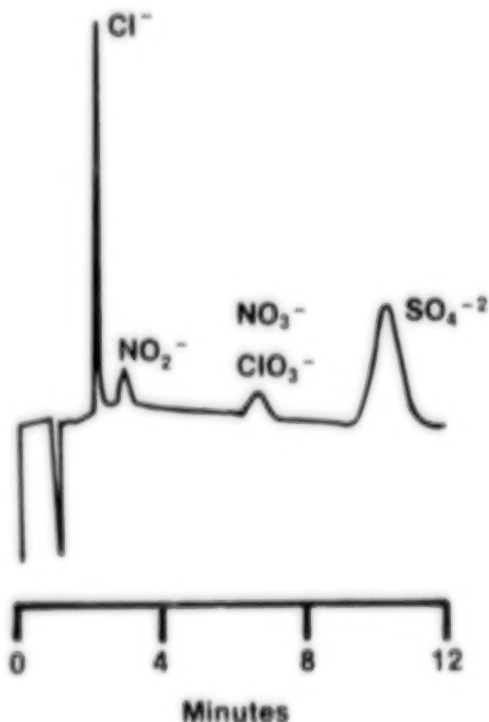


Figure 5. IC Anion Pattern for Pyrodex Combustion Residue.

# **KClO3/Sugar Residue**



Figure 6. IC Anion Pattern for Potassium Chlorate/Sugar Combustion Residue.

is the main combustion product of perchlorate which is present in the Pyrodex. There was also present nitrite, nitrate and sulfate to give a very characteristic pattern for Pyrodex. Actually the peak that is identified nitrate could also be all or partly chlorate as chlorate and nitrate elute at the same time. This problem will be addressed when the UV detector is discussed later.

Figure 6 is the chromatogram of the anion pattern of the residue from the 50/50 mixture of potassium chlorate and sugar. There is a very strong chloride peak and a significant amount of unreacted chlorate. There can be no question that this peak is chlorate because there is no nitrate present in the organical explosive mixture. This is best shown in Figure 7-a,b which illustrates the use of the UV detector in these analyses.

Figure 7-a shows the common anions that are absorbers in the UV at 210nm. Only nitrite, bromide and nitrate absorb, chloride, chlorate and sulfate do not. Figure 7-b shows the chlorate/sugar residue from Figure 6 as detected by the UV detector. No peaks are present.

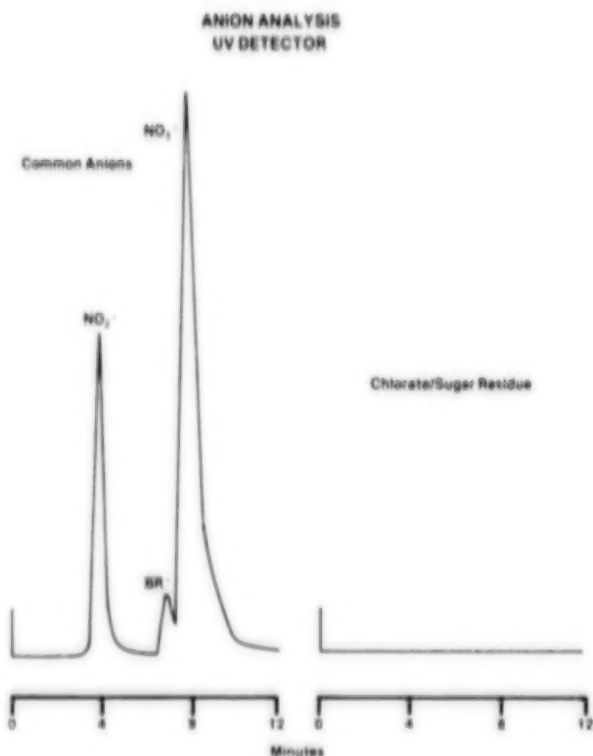


Figure 7. a,b. (a) Separation of Common Anions Using a UV Detector. (b) UV Detection of Chlorate/Sugar Residue.

Figure 8-a,b shows the anion pattern for Pyrodex as detected by the UV detector. Figure 8-a is the actual chromatogram showing some organics from the Pyrodex that also absorbed along with the nitrite and nitrate. As noted previously the nitrate peak in the Pyrodex residue could actually be a mixture of chlorate and nitrate. Figure 8-b shows by the dotted line the height the

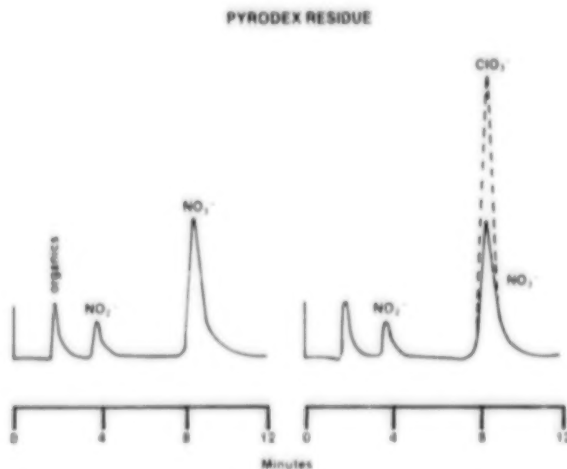


Figure 8. a,b. (a) IC Anion Pattern for Pyrodex Residue Using UV Detection. (b) Theoretical Limits of Chlorate Ion Which is not Detected by the UV Detector.

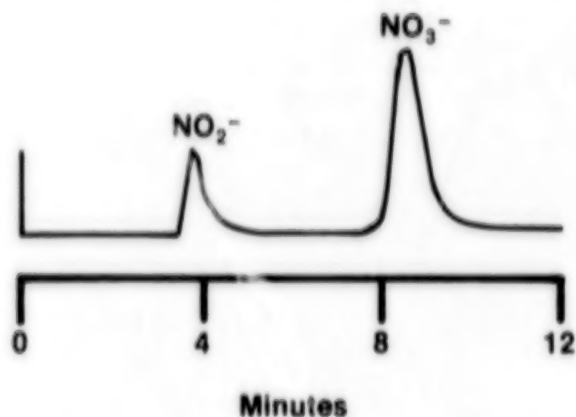


Figure 9. IC Anion Pattern for Black Powder Using UV Detection.

nitrate-chlorate peak should be based on a calculation of the nitrate peak using the conductivity detector. Chlorate is evidently formed from the perchlorate and constitutes about half of the nitrate-chlorate residue.

The Pyrodex residue differs from the black powder residue as detected by the UV detector, because the black powder residue shows no organic peak. Figure 9 shows the anion pattern of black powder using the UV detector. Compare Figure 9 with the black powder anion pattern (homemade) from the conductivity detector, Figure 3.

Using both the conductivity and UV detector (which physically is on line, downline from the conductivity detector, see Figure 1) a very characteristic pattern for the four explosive's residues can be obtained. These patterns can in turn be used to identify a particular explosive. This is the object of establishing a pattern characteristic of each individual low explosive.

The next aspect of the study was to look at the cation pattern for the various low explosives. Of special interest was to determine if any ammonium salts were formed. Figure 10 shows the separation of some common cations and was used as a standard. Figures 11, 12 and 13 shows the cation patterns of the four explosive residues. No significant ammonium was formed in any of the combustion products. The Pyrodex residue showed slightly higher levels of sodium than the other residues but even this is not significant. Other than this difference there is little in the cation patterns to be of value in distinguishing the four explosives tested.

Having established an anion pattern for the four low explosives another test was conducted in which this information could be applied to a case-like situation. Figure 14 is a photograph of a

# STANDARD CATIONS

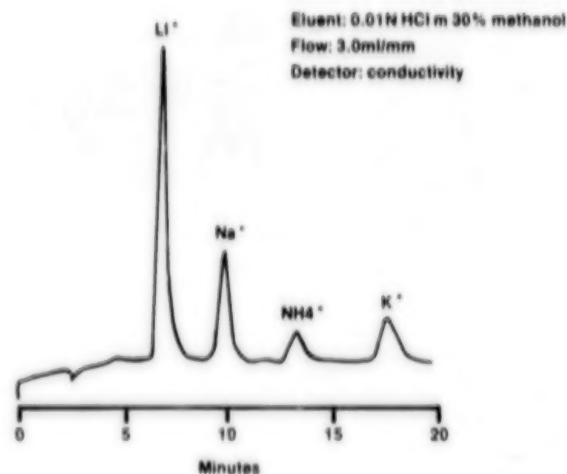


Figure 10. Separation of Common Cations. Peaks:  $\text{Li}^+$ , 10ppm;  $\text{Na}^+$ , 10 ppm;  $\text{NH}_4^+$ , 10 ppm;  $\text{K}^+$ , 10ppm.

# PYRODEX RESIDUE

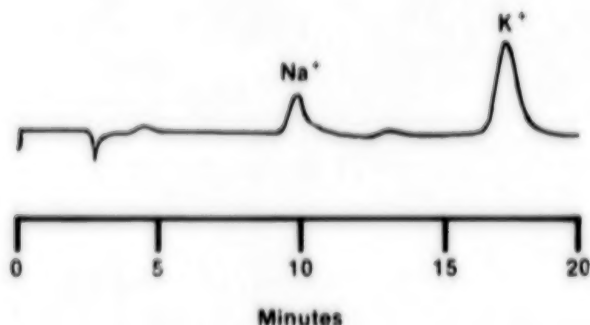


Figure 12. IC Cation Pattern for Combustion Residues of PyroDEX.

# BLACK POWDER RESIDUES

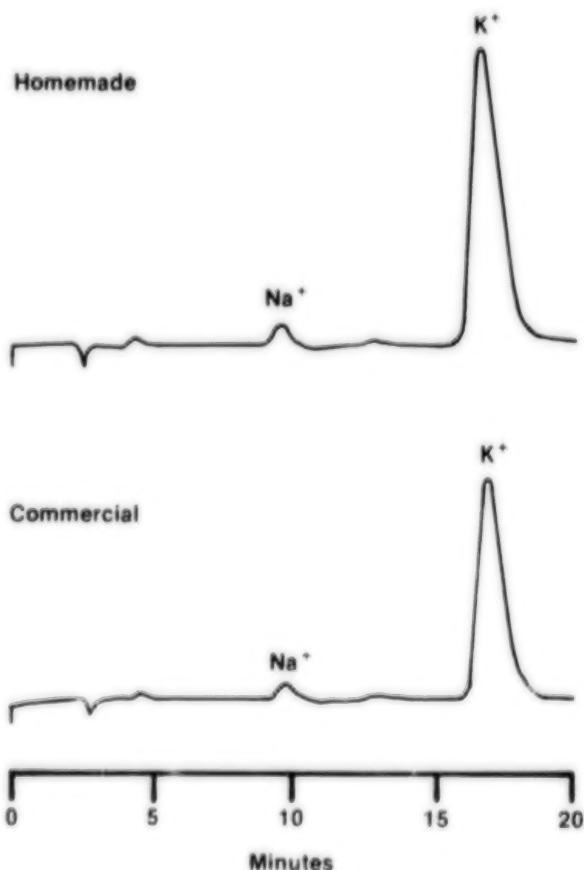


Figure 11a,b. IC Cation pattern for Combustion Residues of (a) Home made Black Powder (b) Commercial Black Powder.

pipe fragment taken from an exploded pipe bomb which contained an unknown low explosive. The fragment was washed with 5ml. of distilled water and after filtering was analyzed by IC.

Figure 15-a shows the water wash of the metal fragment while Figure 15-b shows the anion pattern of the potassium chlorate/sugar mixture. As can clearly be seen they are very similar. Figure 15-a shows no similarity to any of the other anion patterns.

A similar test was conducted with another pipe bomb containing another unknown explosive. A pipe fragment from the exploded pipe (Figure 16)

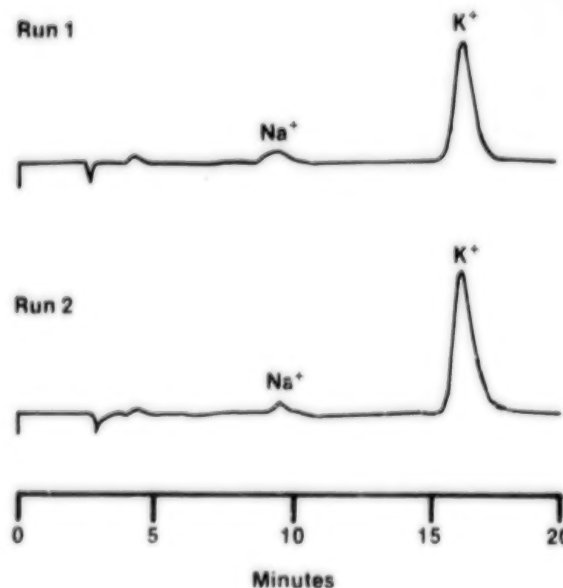


Figure 13. IC Cation Pattern for Combustion Residues of a 50/50 Chlorate/Sugar Mixture for Two Separate Tests.



Figure 14. Photograph of Pipe Bomb Fragment.

was washed and analyzed by IC. Figure 17-a,b shows the results of this test. Figure 17-a is the chromatogram of the unknown residue which composes very favorably with a known Pyrodex residue anion pattern.

A third test was conducted with a firecracker. Figure 18 pictures the type of firecracker on which the test was conducted and a small paper fragment which resulted from exploding a similar one. This small paper fragment was washed with 5ml. of water and the anion analysis conducted. Figure 19-a shows the anion pattern of the firecracker. Of unusual interest is the intense concentration of nitrate in relation to sulfate. There is a difference



Figure 16.

in this pattern when compared to a known black powder anion pattern (Figure 19-b). One explanation of this difference is that there is incomplete combustion in the firecracker of the black powder yielding more unreacted nitrate than residue sulfate. This is not uncommon when such small mixtures of low explosives like black powder are used in a firecracker.

In as much as the pattern failed to match any of the other low explosive, and the absence of any significant chloride peak which would be indicative of a chlorate or perchlorate based explosive, it was determined the firecracker contained a black powder mixture. A check of the pre-blast mixture revealed in fact it did contain black powder.

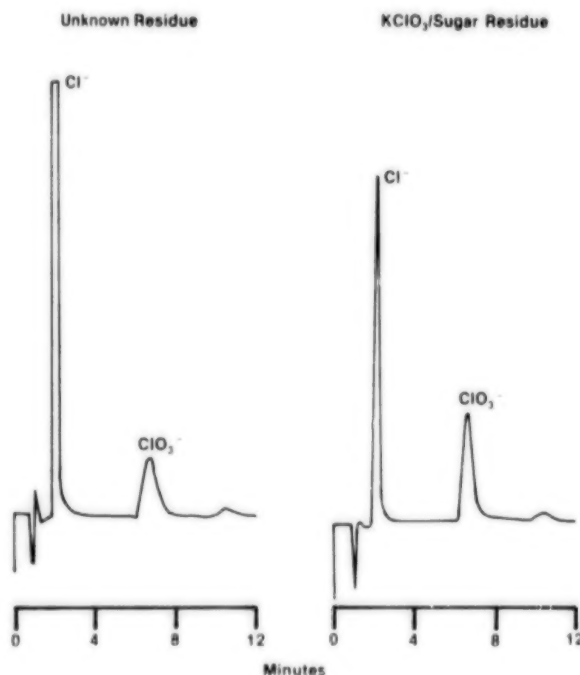


Figure 15a. (a) IC Anion Pattern for Unknown Residue (b) IC Anion Pattern for Pyrodex Residue.

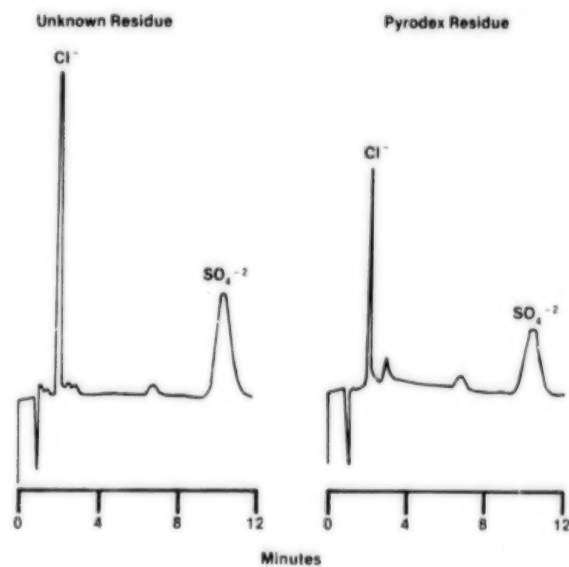


Figure 17.





Figure 18. Photograph of Firecracker and Paper Fragment.

These three examples illustrate the value of IC in analyzing explosive residues. In many cases the bomb crime scene is covered with debris of all sorts, which can act as contaminants in any analysis. IC analysis permits taking a small fragment from the device, which is free of contamination and determining what the explosive main charge was. Although it is often difficult to find large pieces of a contaminant free device, it is not too difficult to find a dime size piece, free of contamination.

The last two figures, Figures 20 and 21 show the relative similarity in several different tests of commercial and homemade black powder. With the exception of the pattern from the 10/28 test date (Figure 21) which shows a large amount of nitrate in the residue, virtually all the patterns are very similar. The difference in the 10/82 test date as we have noted previously can be due to incomplete

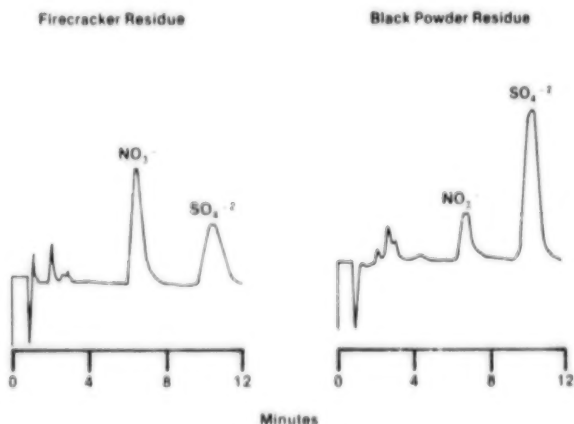


Figure 19. (a) IC Anion Pattern for Residue from Firecracker Paper (b) IC Anion Pattern for Black Powder Residue.

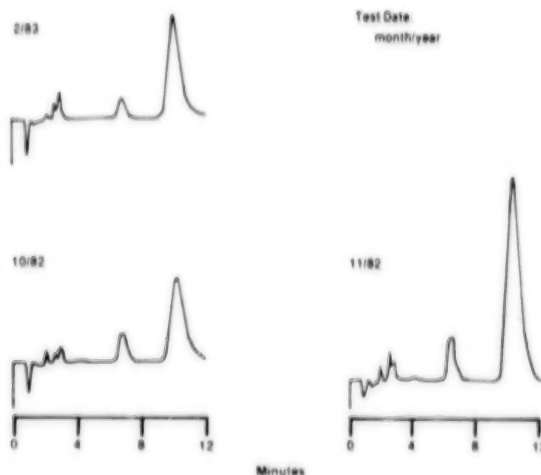


Figure 20. IC Anion Pattern for Commercial Black Powder Residues FOR THREE DIFFERENT TESTS.

combustion occasionally seen in homemade black powders.

In conclusion, it has been demonstrated that IC is a viable method for the evaluation and determination of some low explosives. By developing an anion pattern characteristic of the low explosive identifications can be made of the individual explosives. Of the three basic explosives tested, black powder, Pyrodex, and chlorate/sugar all gave a fingerprint anion pattern which are individually unique.

In the future more testing of other low explosives will be conducted and additionally the formation of sulfide and thiocyanate will also be examined. Due to problems experienced with the Dionex Electrochemical Detector these evaluations were not completed during this series of tests. It is conceivable that through the evaluation of sulfide and thiocyanate levels that commercial and homemade black powder residues could be differentiated.

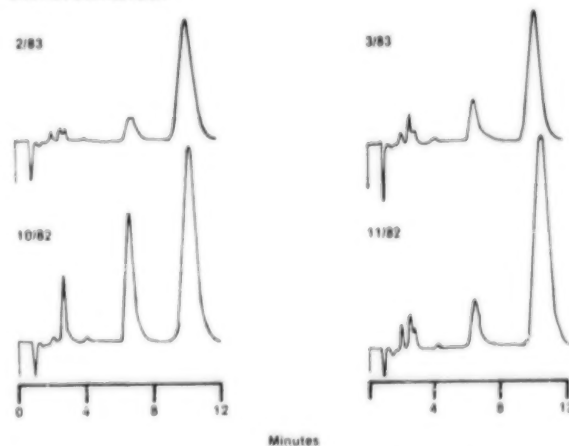


Figure 21. Anion Pattern for Home made Black Powder Residues FOR FOUR DIFFERENT TESTS.

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# IDENTIFICATION OF MONOMETHYLAMINE NITRATE AND MONOETHANOLAMINE NITRATE BY THIN LAYER CHROMATOGRAPHY

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**ABSTRACT.** The sensitizers, monomethylamine nitrate (MMAN) and monoethanolamine nitrate (MEAN), contained in duPont and Hercules water gel explosives respectively, can be uniquely identified in evidentiary samples from bombings by utilizing the three thin layer chromatography (TLC) systems discussed in this paper. These TLC methods also identify the presence of other explosive ingredients and contaminants commonly found in debris from bombings.

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## INTRODUCTION

The identification of explosive residue in evidentiary samples from bombings, has been complicated by the proliferation of dynamite substitutes. Explosives sensitized with nitrostarch, nitrocellulose, ethylene glycol mononitrate, aluminum, and alkylammonium nitrates are displacing explosives sensitized with nitroglycerin and nitroglycol. For example, in the mid-1970's DuPont discontinued the manufacture of explosives containing nitroglycerin in favor of water gels. Parker (1975)

Unlike most other ingredients in commercial explosives, these modern sensitizers are often unique to explosives produced by one manufacturer, for example:

—DuPont uses methylammonium nitrate (monomethylamine nitrate or MMAN)

—Hercules uses ethanolammonium nitrate (monoethanolamine nitrate or MEAN)

—Trojan used nitrostarch

Thus, the type of explosive and its manufacturer can be identified if these sensitizers are detected.

This paper describes thin layer chromatography

systems by which the currently used alkylammonium nitrate sensitizers MMAN and MEAN can be uniquely identified.

## EXPERIMENTAL PROCEDURE

When initial visual and microscopic examinations of debris fail to reveal the presence of an explosive, then the entire sample of debris is extracted. The debris can first be extracted with distilled water and secondly with acetone or methanol. The extracts are filtered and evaporated to dryness. The water extract is redissolved in a small quantity of water for chemical spot tests. Feigl (1956) If the presence of nitrite or nitrate ions is detected with the Griess spot test, then the water and/or methanol extracts may contain MMAN or MEAN. These extracts are then prepared for TLC analysis by adding a few drops of the extracting solvent to the respective extract in order to redissolve and concentrate the explosive residue. The three TLC systems utilized in this procedure are shown in Table I.

Table I

System	Development Solution	Plate	Sprays
I	chloroform/methanol/water (100:90:14)	K2	diphenylamine or ninhydrin
II	chloroform/methanol (7:3)	K5	fluorescamine visualization
III	chloroform/100% ethanol/water/HCl (100:90:5:3.5)	K5	ninhydrin

Screening for alkylammonium nitrates and confirming the presence of ammonium, sodium, and potassium ions is performed using TLC System I. Primary amines and amino acids are visualized by spraying with ninhydrin. The ninhydrin solution consists of 0.2% ninhydrin in 0.1M citric acid, adjusted to pH 5 with 2.0 N sodium hydroxide. Feigl (1956) Plates sprayed with ninhydrin are heated at 100° C for 7 to 10 minutes to develop the color. The limits of detection for MMAN and MEAN, when sprayed with ninhydrin, are about 0.5 ug. Nitrates are detected by spraying the plates with a solution of 5% diphenylamine (DPA) in 95% ethanol followed by 10 minutes exposure to ultraviolet light and then spraying the plates with concentrated sulfuric acid. Parker *et al.* (1975). The limits of detection for MMAN and MEAN, when sprayed with the diphenylamine/sulfuric acid combination are about 1.0 ug. Due to interferences which may arise in this TLC system from some compounds (notably calcium salts from soil or explosives), and uncertainty in distinguishing MMAN and MEAN from each other, it may be necessary to also use one of the other TLC systems, for the confirmation of MMAN and MEAN.

If screening by System I indicates the presence of MMAN or MEAN, then fluorecamine derivatized amines are separated using System II. Primary amines and amino acids form intensely fluorescent substances when reacted with fluorecamine. This reaction proceeds rapidly at room temperature at pH 9. A solution of fluorecamine is prepared by dissolving 50 mg. of fluorecamine in 100 ml. of acetone. A 0.2 M borate buffer solution is also prepared by dissolving 1.24 g boric

acid in 100 ml distilled water. The pH of this solution is adjusted to 9.0 by titrating with sodium hydroxide. Nowicki (1976) A few drops of the redissolved extract solution are placed into a well of a porcelain spot plate. Into each of these wells, two drops of the borate buffer solution are added followed by one drop of the fluorecamine solution. Upon completion of the reaction, the solutions are examined under ultraviolet light to observe the fluorescence. Those solutions which react positively are spotted on K5 TLC plates and developed utilizing System II. The limit of detection for MMAN and MEAN is about 2.0 ug. This system gives an excellent separation of MMAN from MEAN. While MEAN and ammonia produce spots having similar Rf's with this system, they can be distinguished from one another by using System III.

System III, although slow, separates MMAN from MEAN with no interference from ammonia. Plates developed using this system are sprayed with ninhydrin. The developing solution must be prepared using 100% ethanol and concentrated HCl since this system is sensitive to the concentration of water. The loss of HCl and the uptake of water reduce the efficiency of this solvent in three or four weeks. This system is especially useful when MMAN or MEAN are in very low concentrations in the extract and may fail to be detected with System II. However, while high concentrations of amino acids streak in System III and can obscure the presence of MMAN and MEAN, amino acids remain at the origin in System II, thus eliminating their interference with MMAN and MEAN. Data for these three systems is presented in Table 2.

Table 2 \*RF's (as%)

Solvent System	System I	System II	System III
TLC Plate	K2	K5	K5
Compound			
MMAN	40-56	60	31-37
MEAN	33-47	39	18-28
Ammonium Nitrate	31-46	40	
Sodium Nitrate	17-31	—	
Potassium Nitrate	10-14	—	
n-Ethylammonium NO <sub>3</sub>	61-72		37-38
n-Propylammonium NO <sub>3</sub>	66-72	73	41-51
n-Amylammonium NO <sub>3</sub>	77-88	69	48-66
Iso-Propylammonium NO <sub>3</sub>	26-29		41-55
Iso-Butylammonium NO <sub>3</sub>	69-82		
1-amino-2-propanol NO <sub>3</sub>	52-61	54	36-38
2-amino-1-propanol NO <sub>3</sub>	41-56	42	41-43
2-amino-1-butanol NO <sub>3</sub>	55-68	53	41-45

Table 2 \*Rf's (as %)—Cont.

Solvent System	System I	System II	System III
TLC Plate	K2	K5	K5
Anthranalic acid	95-97		95-97
Phenylalanine	44-67	0	5
3,4-Dihydroxyphenylalanine	1	0	49
Tryptophan	0-28	0	50
Tyrosine	0	0	50
Norvaline	40-61	0	50
Ethionine	47-61	0	49
Isoleucine	52-63	0	49
Leucine	47-78	0	50
Methionine	4-54	0	50
Alanine	14-27	0	41
Arginine	0	0	24-3
Asparagine	0	0	19-24
Aspartic acid	0	0	49
Citrulline	0	0	3-38
Cystine	0	0	25-28
Glutamine	5-14	0	49
Glycine	1	0	28-41
Histidine	0	0	16-23
Lysine	1	0	14
Norleucine	61-75	0	50
Proline	33-42	0	50
Serine	10	0	38-43
Threonine	0-22	0	
Valine	36-61	0	50
3-Phenyl-1-propylamine			69-76
2-Amino-1-phenylethanol			69-76
Phenethylamine			69-74
Methamphetamine			70-75
Dextroamphetamine			65-70

\*Rf's are recorded as the Rf of the tail and the Rf of the leading edge.

\*tert amines, secondary amines, aniline, guanidine, hexamine, hydroxylamine, diphenylamine, urea, uric acid, etc., do not react with ninhydrin.

## CONCLUSION

The use of these three TLC systems provides the necessary data for the unique identification of MMAN and MEAN. Ninhydrin and fluorescamine react with the primary amines. The diphenylamine/sulfuric acid spray combination and Griess spot test identify the presence of nitrate ions. The use of three different TLC systems increases specificity. In Systems I and III, compounds larger than ethanolamine nitrate, such as nitrates of alkylamines, alkylamine alcohols, and arylamines, have greater Rf values than MMAN or MEAN. System II provides the separation of MMAN and MEAN from amino acids which remain at the origin.

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## **MASS SPECTROMETRY METHODS**



## ANALYSIS OF EXPLOSIVES BY LC/MS

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**ABSTRACT.** In many applications of forensic analysis, an analytical method is required which combines good separation characteristics with highly specific and sensitive detection. The Liquid Chromatography/Mass Spectrometry (LC/MS) system has such specifications and has an advantage over GC/MS in that it is suitable for thermally sensitive and involatile compounds. We have interfaced an HPLC with a magnetic sector mass spectrometer. The mass spectrometer is a home built 90° 4-inch radius magnetic sector instrument with a high-speed differential pumping system. The HPLC consists of an Eldex High Pressure Pump, an Eldex Solvent Programmer, a Rheodyne Model 7125 Sample Injector and a Waters 441 UV Detector. The column used was a RP-8 reversed-phase column. Mobile phases were methanol/water and acetonitrile/water at various relative concentrations. The LC/MS interface is a commercial Hewlett-Packard Direct Liquid Insertion Probe LC/MS Interface which is a variable split-type interface. A series of standard explosive mixtures including TNT, RDX, Tetryl, NG and DEGN, as well as commercial explosives have been analyzed by this LC/MS system. LC/MS spectra of these explosives will be shown in order to demonstrate the usefulness of this technique in forensic analysis.

When we talk about LC/MS, we have in the back of our mind GC/MS, which has achieved a remarkable success in qualitative and quantitative analysis. However GC has its limitations: GC, and therefore GC/MS is not suitable for thermally sensitive and involatile compounds, although techniques have been evolved to minimize these problems.

HPLC however, has been shown to be a successful separation technique for thermally labile compounds. Judging from the number of papers on HPLC in this symposium it certainly is a suitable method for the analysis of explosives.

The main problem in LC/MS is to match a liquid at high pressure with the high vacuum of the mass spectrometer. An HPLC flow rate of 1 ml/min results in a gas volume of 150-1200 ml/min, depending on the solvent used. A CI mass spectrometer can handle about 20 ml/min.

Several interfaces have been designed [McFadden (1979)], some of them are already commercially available. We have used in our system the Hewlett-Packard Direct Liquid Insertion Probe Interface [Matera (1980)] which is shown schematically in Figure 1. The LC effluent enters the

interface and is split at the entrance of the ion source. Only about 1-2% of the effluent is allowed to enter the mass spectrometer, through a 5µm aperture made in a stainless steel diaphragm. The droplets of the jet thus formed, are vaporized in a desolvation chamber, after which the solvent/sample vapor enters the ion source. The sample is ionized, the solvent serving as chemical ionization (CI) reagent.

The advantages of this interface are its relative simplicity and the fact that it can be used also for reversed-phase HPLC. Sample and solvent enter the desolvation chamber as droplets, which gives the sample a certain protection against thermal fragmentation prior to ionization. We obtain some type of direct chemical ionization, which makes this method in particular suitable for thermally labile compounds. The main disadvantage is that because of the effluent split, the sensitivity is reduced. The mass spectrometer we are using is a home built 90° 4-inch radius magnetic sector instrument with a high-speed differential pumping system. The HPLC consists of an Eldex A-30-5 pump, an Eldex programmer and low pressure valve, a Rheodyne 7125 Injector and a Waters 441

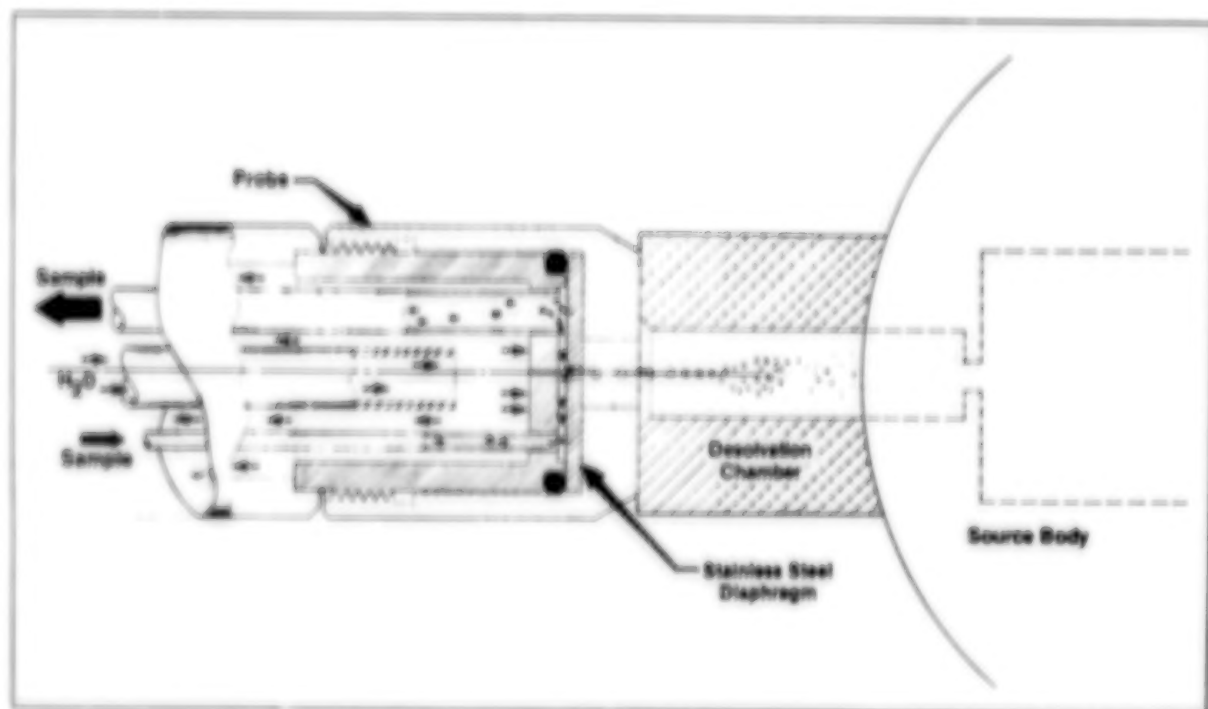


Figure 1. Direct liquid insertion probe interface.

UV Detector.

Figure 2 shows the entire LC/MS system while Figure 3 gives an insight into the ion source region through the glass seal.

The heated desolvation chamber is made of MACOR glass-ceramic and serves as electrical insulation between the ion source which is at 1500 Volts and the grounded interface probe. We have a cold finger cooled by liquid nitrogen to provide extra cryogenic pumping, but we have found that the system can also be operated without a cold finger. The performance of the system was found to be optimal when the source was not entirely closed, so that the local pressure in the ion source was not too high. This was achieved by having an opening in the source or by keeping the Interface Probe at a certain distance from the desolvation chamber. Although there is a high voltage insulation between the source and the interface probe, voltage breakdowns sometimes occur. The solvent vapor serves as electrical conductor. With acetonitrile less breakdowns occur than with methanol. This problem does not exist in quadrupole mass spectrometers where the ion source is at ground potential or at low voltage. The HPLC column used was a Brownlee RP-8 reversed-phase column, Lichrosorb 10 $\mu$ m particle size, 4.6 mm x 10 cm length. Mobile phases were methanol:water and acetonitrile:water at a flow rate of 1 ml/min.

UV detector wavelength was 214 nm.

When using the direct-injection type interface, we must be aware that large amounts of solvent but only a small amount of sample are introduced in the source. Solvent peaks can interfere with sample peaks, therefore the exact mass spectra of the solvents have to be known.

Figures 4 and 5 show respectively the high pressure mass spectra of acetonitrile:water (50:50) and methanol:water (50:50). Part of the mass spectrum in Figure 5 has been upscaled in order to demonstrate the possibility of solvent peaks interfering with sample peaks which are in the same mass range. Earlier experiments on the analysis of explosives by LC/MS have been done using negative ions [Parker, Voyksner, Tondeur, Henion, Harvan, Hass and Yinon (1982)] and positive ions [Yinon (1983)].

The following examples demonstrate the use of this system for the analysis of several technical and standard mixtures.

Figure 6 shows the HPLC-UV trace of a technical mixture containing TNT + RDX with acetonitrile:water (50:50) as mobile phase. Figures 7 and 8 show respectively the LC/MS mass spectra of TNT and RDX. The mass spectrum of TNT includes the MH<sup>+</sup> ion at m/z 228, typical adduct ions (M + CH<sub>3</sub>CN + H)<sup>+</sup> at m/z 269 and (M + 2CH<sub>3</sub>CN + H)<sup>+</sup> at m/z 310, an EI fragment

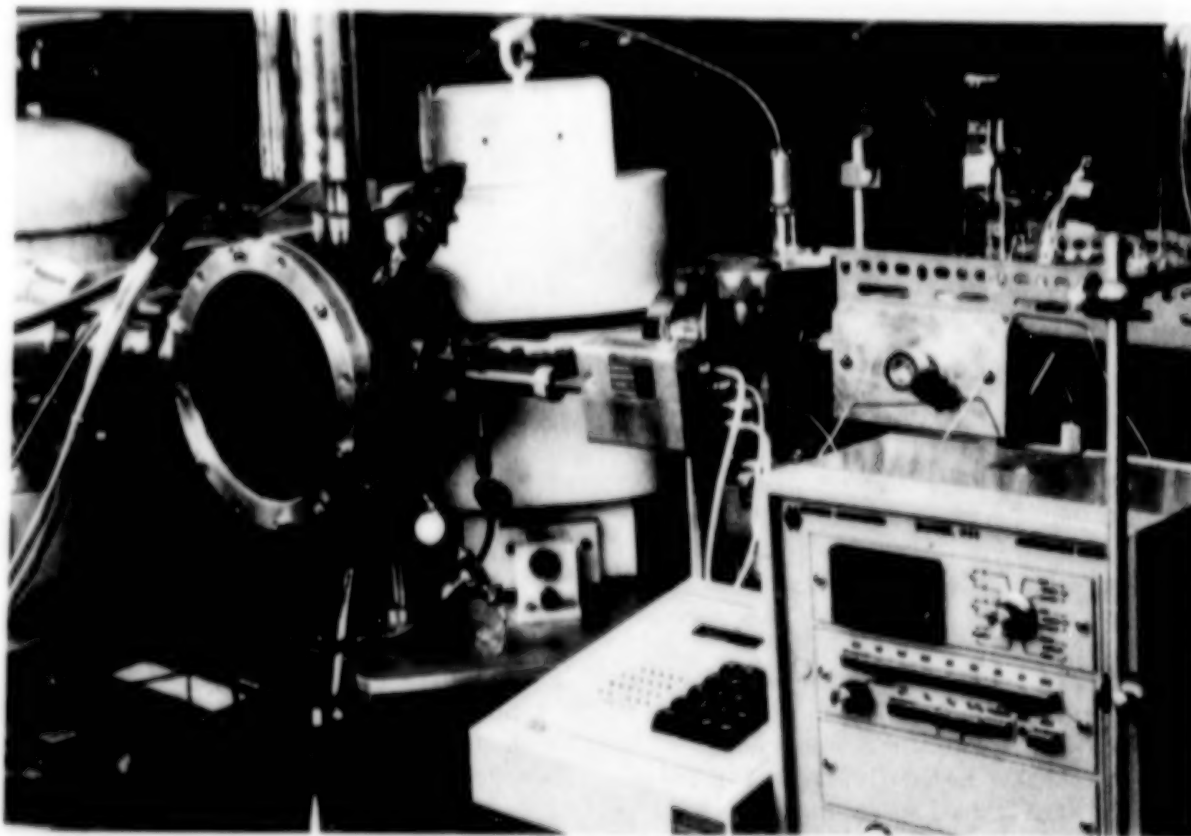


Figure 2. LC/MS system.

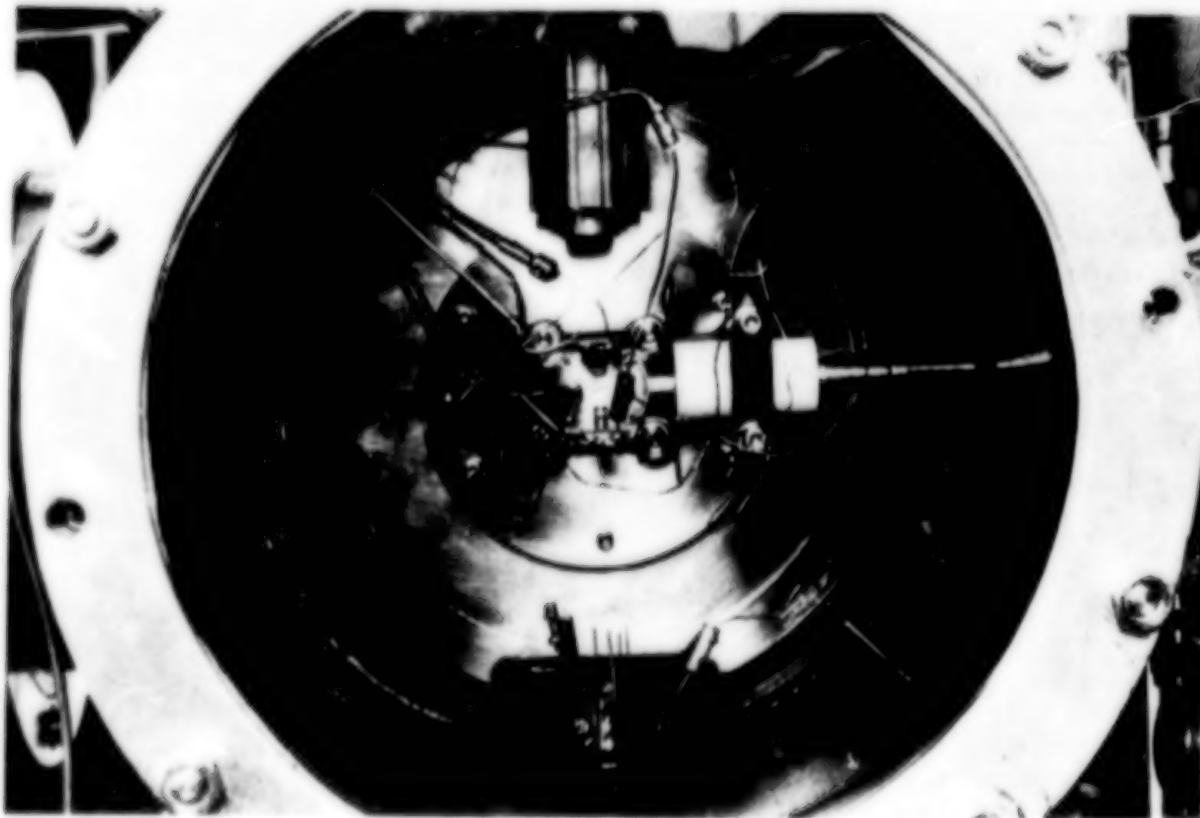


Figure 3. Ion source of LC/MS system.

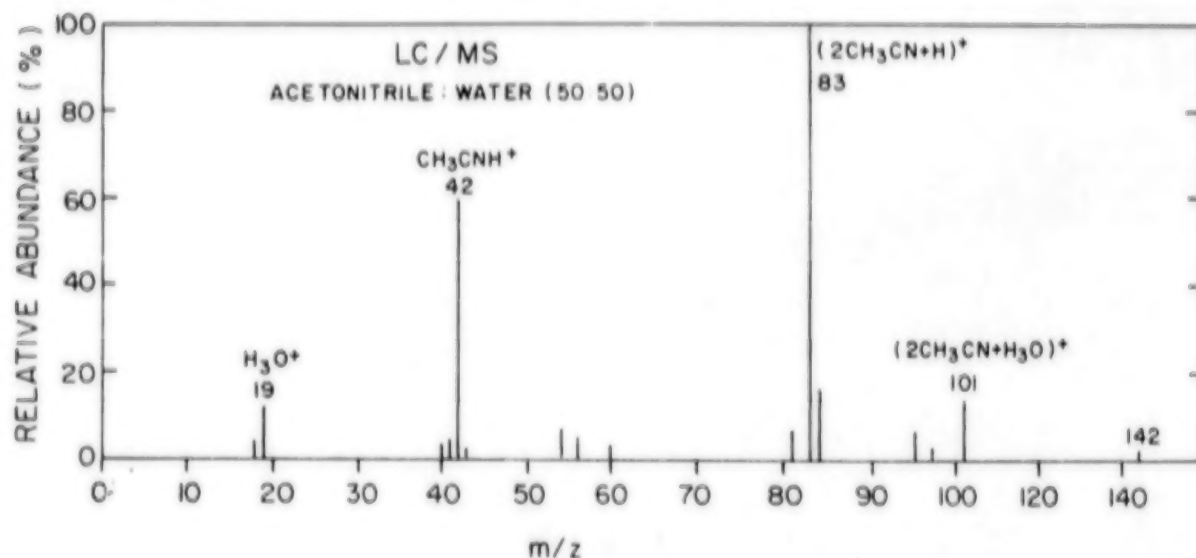


Figure 4. High pressure mass spectrum of acetonitrile:water (50:50).

ion  $(M-OH)^+$  at  $m/z$  210 and an abundant fragment ion  $(MH-30)^+$  at  $m/z$  198 mainly due to the reduction process to the corresponding amine [Yinon and Laschever (1981)] and partly to  $(MH-NO)^+$ . The mass spectrum of RDX includes the  $MH^+$  ion at  $m/z$  223, the  $M^+$  ion at  $m/z$  222, the adduct ions  $(M+NO)^+$  at  $m/z$  252 and  $(M+CH_3CN+H)^+$  at  $m/z$  264 and typical fragment ions  $(M-NO_2)^+$  at  $m/z$  176 and  $(MH-CH_2N_2O_2)^+$  at  $m/z$  149.

Figure 9 shows the HPLC-UV trace of a technical mixture containing RDX + PETN, using acetonitrile:water (50:50) as mobile phase. The mass spectrum of RDX is similar to the one in Figure 8. The LC/MS mass spectrum of PETN (Figure 10) contains the  $MH^+$  ion at  $m/z$  317 which can clearly

be seen above the background noise.

Figure 11 shows the HPLC-UV trace of a standard mixture of TNT and tetryl using methanol:water (50:50) as mobile phase. Figures 12 and 13 show respectively the LC/MS spectra of TNT and tetryl. The mass spectrum of TNT includes the  $MH^+$  ion at  $m/z$  228, an adduct ion  $(M+CH_3OH+H)^+$  at  $m/z$  260, the  $M^+$  ion at  $m/z$  227 and the EI fragment ion  $(M-OH)^+$  at  $m/z$  210 and the ion  $(MH-30)^+$  at  $m/z$  198. No molecular ion was observed in the mass spectrum of tetryl, but only characteristic fragment ions at  $m/z$  241  $(M-NO_2)^+$ ,  $m/z$  225  $(M-NO_3)^+$  and  $m/z$  224  $(M-HNO_3)^+$ . Figure 14 shows the HPLC-UV trace of a standard mixture of nitroglycerin (NG) and diethylene glycol dinitrate (DEGN) using

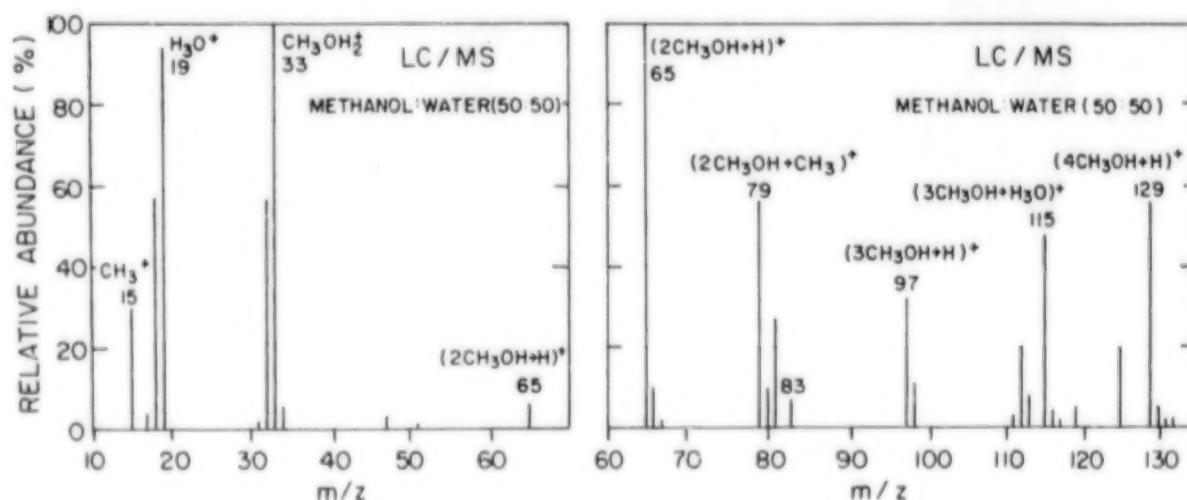


Figure 5. High pressure mass spectrum of methanol water (50:50).



# HPLC-UV TRACE OF TECHNICAL MIXTURE CONTAINING TNT+RDX

COLUMN: RP-8

ACETONITRILE:WATER(50:50),1ml/min.

UV-WAVELENGTH: 214nm

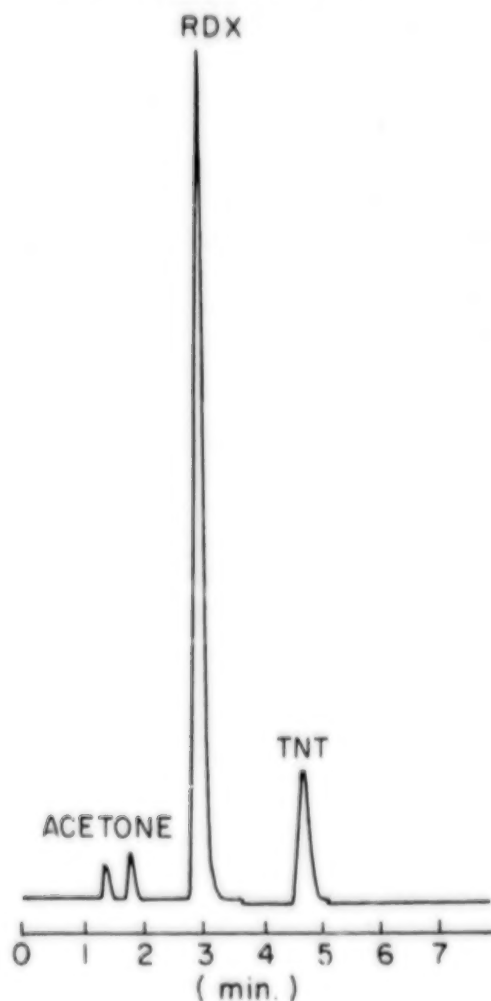


Figure 6. HPLC-UV trace of a technical mixture containing TNT + RDX.

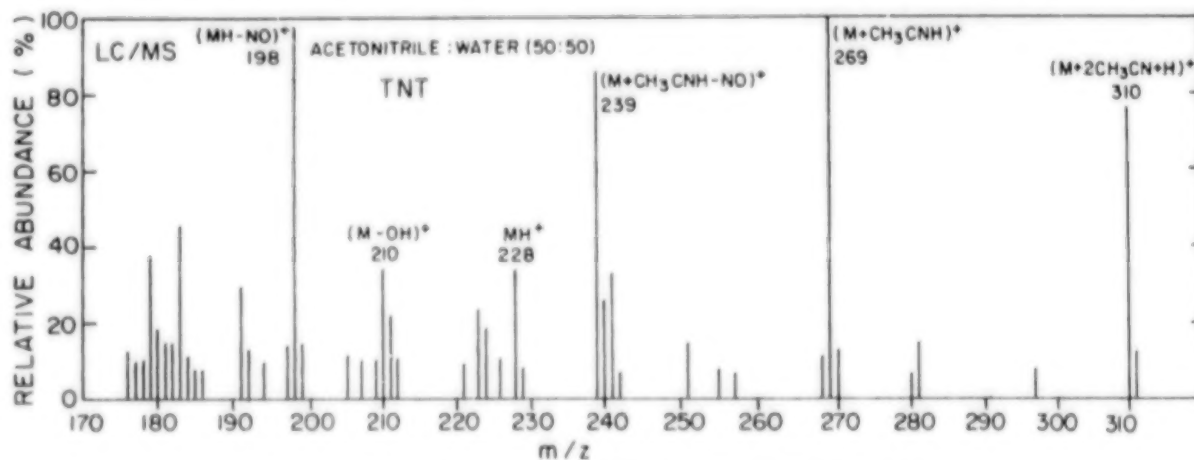


Figure 7. LC/MS mass spectrum of TNT with acetonitrile:water as reagent.

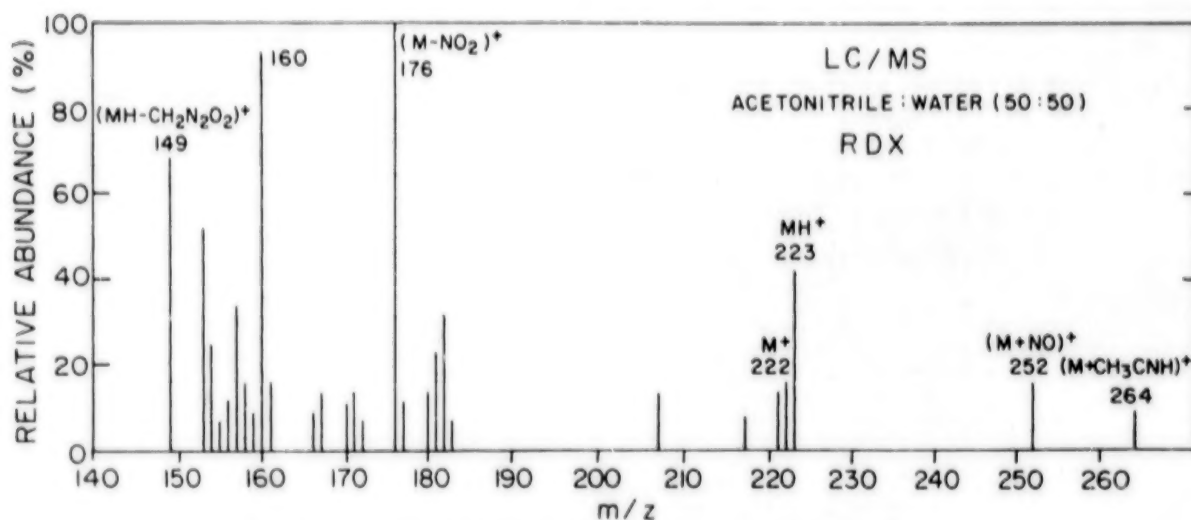


Figure 8. LC/MS mass spectrum of RDX with acetonitrile:water as reagent.

### HPLC-UV TRACE OF TECHNICAL MIXTURE CONTAINING RDX+PETN

COLUMN: RP-8

ACETONITRILE:WATER(50:50),1ml/min

UV-WAVELENGTH: 214nm

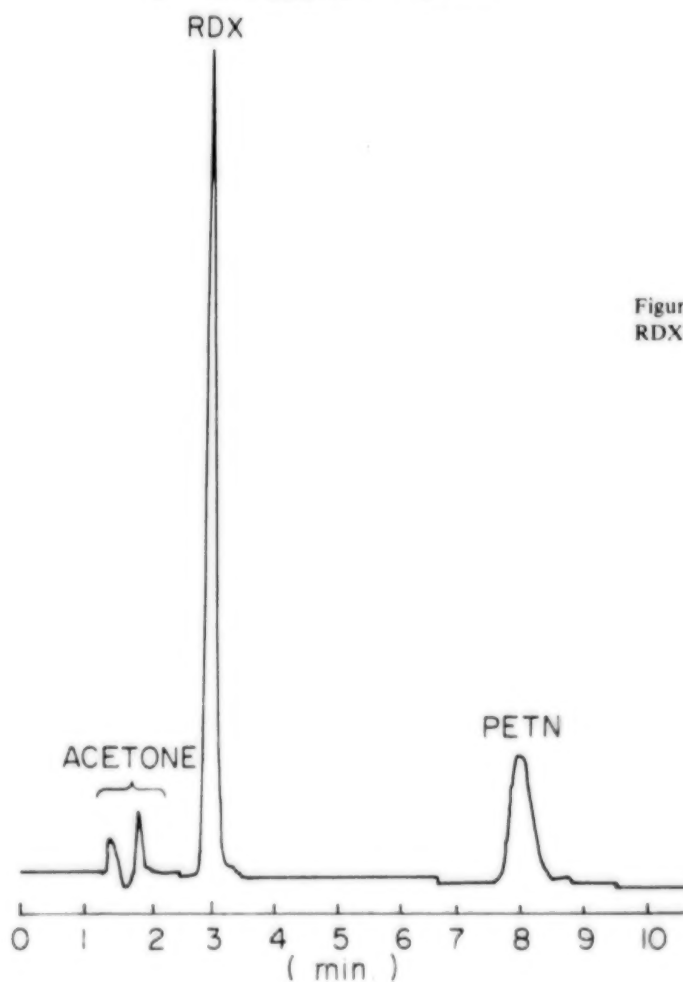


Figure 9. HPLC-UV trace of a technical mixture containing RDX + PETN.

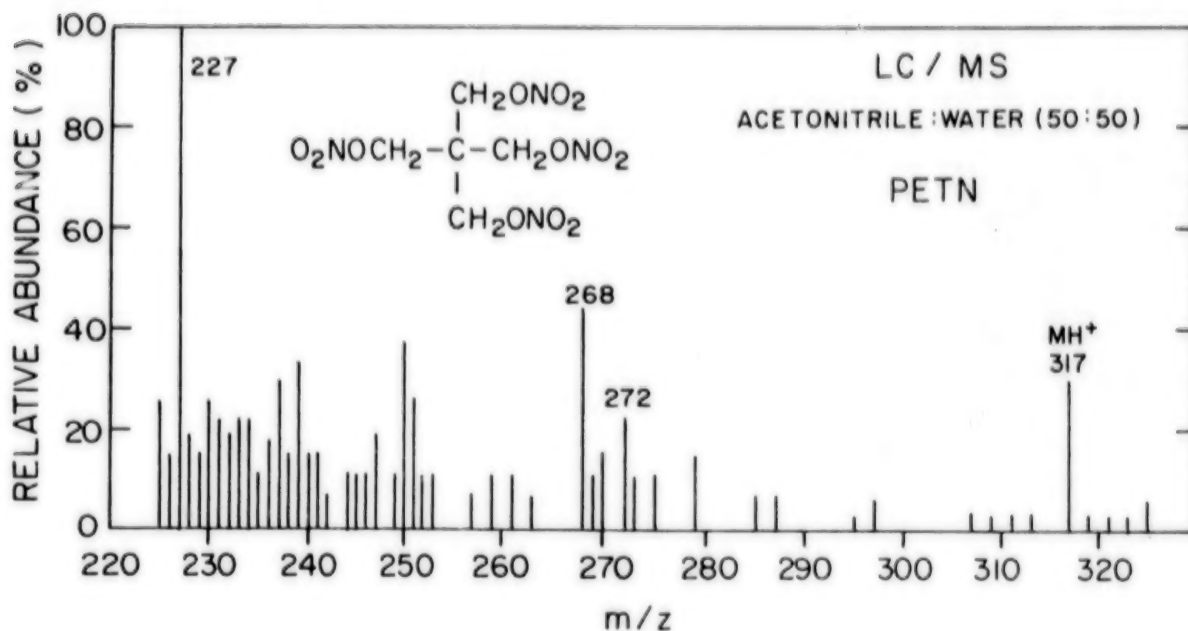


Figure 10. LC/MS mass spectrum of PETN with acetonitrile:water as reagent.

methanol:water (50:50) as mobile phase. Figures 15 and 16 show respectively the LC/MS mass spectra of NG and DEGN. The mass spectrum of NG includes a small  $\text{MH}^+$  ion at  $m/z$  228 and characteristic fragment ions  $(\text{MH}-\text{CH}_3\text{NO})^+$  at

$m/z$  183 and  $(\text{MH}-\text{HNO}_3)^+$  at  $m/z$  165. The mass spectrum of DEGN includes a small  $\text{MH}^+$  ion at  $m/z$  197 and the fragment ions  $(\text{MH}-\text{O})^+$  at  $m/z$  181,  $(\text{MH}-\text{HNO}_3)^+$  at  $m/z$  134 and

## HPLC-UV TRACE OF STANDARD MIXTURE OF TNT AND TETRYL

COLUMN: RP-8

METHANOL:WATER(50:50), lml/min

UV-WAVELENGTH: 214nm

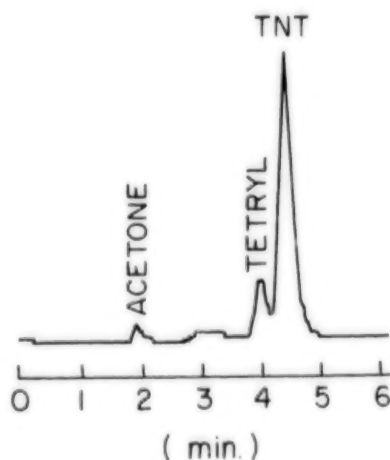


Figure 11. HPLC-UV trace of a standard mixture of TNT and tetryl.

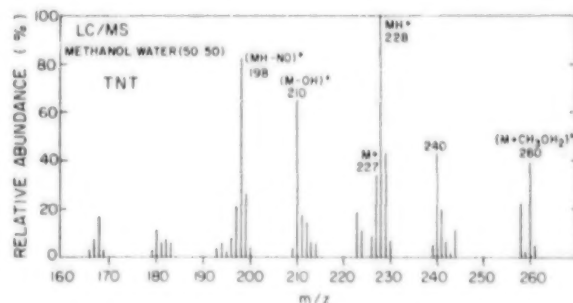


Figure 12. LC/MS mass spectrum of TNT with methanol water as reagent.

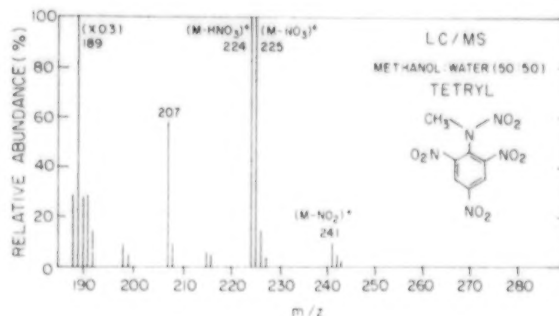


Figure 13. LC/MS mass spectrum of tetryl with methanol:water as reagent.

# HPLC-UV TRACE OF NG+DEGN MIXTURE

COLUMN: RP-8  
METHANOL: WATER (50:50), 1ml/min  
UV WAVELENGTH: 214nm

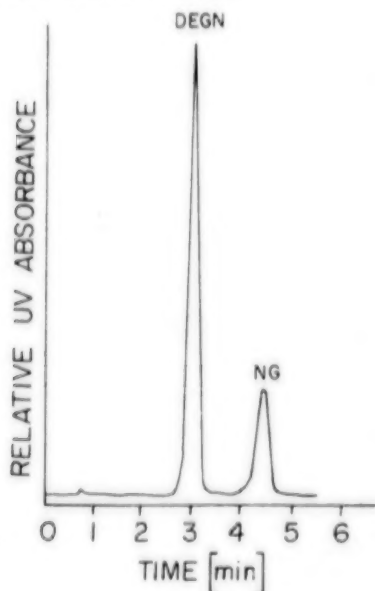


Figure 14. HPLC-UV trace of a standard mixture of NG and DEGN.

$(MH-HONO_3)^+$  at  $m/z$  118 which is the base peak.

## CONCLUSIONS

In the direct liquid introduction method, because only 1% of the effluent enters the mass spectrometer, about 2 orders of magnitude of sensitivity are lost. In our system, in order to obtain an identifiable mass spectrum, we needed to inject in the HPLC between 1-10  $\mu$ g sample. These amounts can be considerably reduced by using integration techniques or single ion monitoring. The Direct Liquid Introduction Interface is simple and can be easily accommodated on any mass spectrometer with very little instrumental modification. The future of LC/MS is in micro LC/MS where flow rates are in the order of 10  $\mu$ l/min and where the entire effluent can enter the ion source without any splitting, and therefore without any loss of sensitivity.

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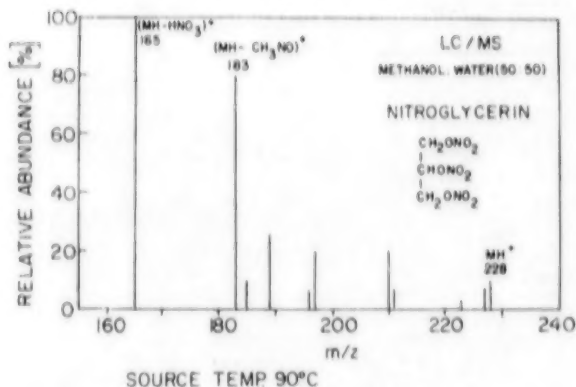


Figure 15. LC/MS mass spectrum of NG with methanol:water as reagent.

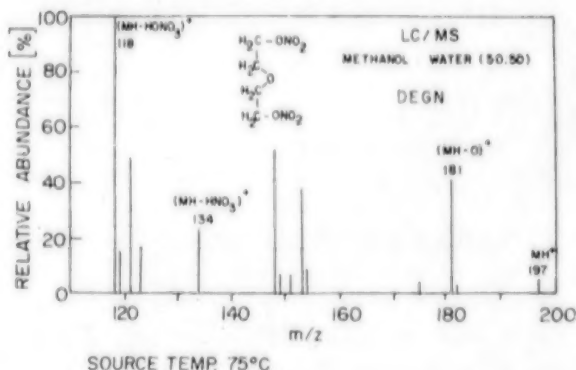


Figure 16. LC/MS mass spectrum of DEGN with methanol:water as reagent.

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## THE ANALYSIS OF POST-DETONATION CARBON RESIDUES BY MASS SPECTROMETRY

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**ABSTRACT.** In the forensic analysis of specimens from scenes of explosions it is normal to find some traces of the undecomposed explosive. However, it has proved impossible to detect and identify 2,4,6-Trinitrotoluene (TNT) in residues by the normal methods of swabbing followed by Gas Chromatography of the extract. As an oxygen deficient explosive TNT deposits carbon in the form of particles on surfaces in the vicinity of the site of the explosion, and it was considered that this carbon could provide a means of identifying the explosive, since decomposition products from the detonation could well be trapped within it. Samples of carbon were examined by Mass Spectrometry using a pyrolysis probe. The detailed method of sample preparation will be described together with an account of the problems encountered. By flash heating the carbon sample in the pyrolysis chamber, which was directly connected to the Mass Spectrometer source, it was possible to examine the materials released. Our initial studies indicated that unreacted TNT was present and could be identified. These preliminary studies produced a success rate of 20% and further work has improved the technique considerably. This has included modifications to the probe design to permit its use in the Chemical Ionisation and Negative Ion modes. The modifications and their effects will be described and the implications for the use of the technique with other carbon depositing explosives such as RDX and PETN will be discussed.

### INTRODUCTION

It is important for forensic purposes to be able to identify the material used in illegal devices. Normally some traces of undecomposed explosive remains after detonation, but it has proved extremely difficult to detect and identify 2,4,6-trinitrotoluene (TNT) by the normal methods of swabbing followed by Gas Chromatography of the extract.

It has been observed that although the detonation of TNT is very efficient, it deposits carbon in the vicinity of the explosion. The deposit normally takes the form of a film or particles of varying sizes. This behavior is also observed with other explosives such as 1,3,4-trinitro-1,3,5-triazacyclohexane (RDX) and tetra-methoxymethane tetranitrate (PETN), though the carbon production is particularly pronounced with TNT, which is oxygen deficient.

It has been postulated (1) that this carbon contains some nitrogen-containing compound or compounds resulting from the thermal decomposition of TNT not involved in the detonation. It has also been observed during in-house studies on the detonation of acetylene that organic materials are found in the carbon deposited by this reaction (Reference 2).

It was considered that an investigation of the carbon deposited could lead to methods for detecting the typical explosion products of TNT and thence identifying it as the explosive found in forensic cases. The principal method used in this investigation was pyrolysis—mass spectrometry, since it was considered that pyrolysis techniques offered the greatest likelihood of success in releasing trapped species held within or on the carbon, and that mass spectrometry would provide the most satisfactory means of identification.

Pyrolysis is a technique which has become established for the characterisation of compounds which are either involatile or possess low volatility, *e.g.* polymers (Reference 3). The Curie Point technique was the method used, in which the sample is mounted on a ferromagnetic pyrolysis wire of known Curie Point. The wire is then placed within an Rf coil which is energised with high frequency current. The hysteresis losses from the induced magnetic field in the wire rapidly (1/2-1s) heat the wire to its Curie point. At this temperature the level of induced flux is considerably reduced giving much reduced heating in the wire. Consequently the temperature of the wire stabilises to within a few degrees of its Curie point as long as the coil is energised.

Different alloys with different magnetic properties have different Curie points, and therefore varying the composition of the wire allows a range of pyrolysis temperatures to be used. A temperature of 1043K is produced by a wire of 100% Fe, while an alloy of 50.6% Fe and 49.4% Ni w/w gives a temperature of 783K.

### EXPERIMENTAL

Mass Spectra were obtained with a VG Micro-mass 16F single focussing magnetic sector instrument. The ion source is fitted with four re-entrants, one for direct liquid injection, one for the solids probe, and two for GC effluents.

Pyrolysis-Mass Spectrometry (py-MS) was carried out with the VG Organic Pyroprobe, using a modified Pye Unicam Rf coil and controller. The probe is inserted through the airlock provided for the solids probe and butts directly on to the source by means of a ceramic cone. Volatile pyrolysis products pass directly through the centre of the probe, as a result of the pressure difference, and enter the source. The probe assembly is shown schematically in Figure 1. The wire is mounted in the holder and fitted with the shield shown in Figure 2, before loading into the probe.

The method of preparing carbon samples for

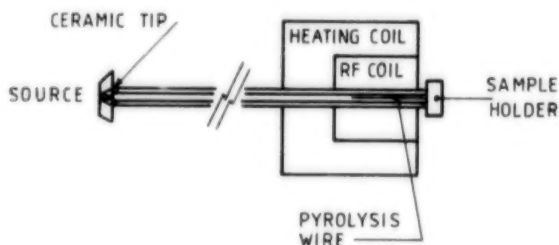


Figure 1 Pyrolysis Probe.

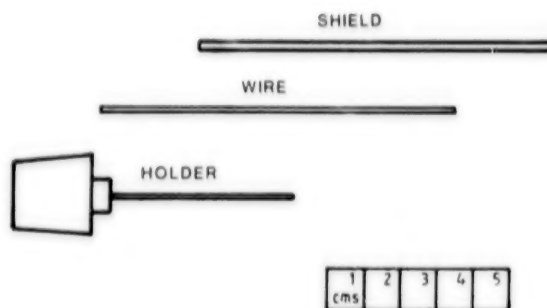


Figure 2

analysis depends on the type of deposition. For example if the carbon particles are deposited on metal surfaces it is relatively easy to scrape them off and test them without further preparation. Two other examples of carbon deposition were studied and methods for sample removal developed:

#### (1) From cloth.

The recovery was carried out as follows:

(a) The samples were cut into small squares (4 cm<sup>2</sup>)

(b) Each sample was held in a No. 4 glass sinter fitted to a Buchner flask under suction and repeatedly washed with distilled water.

(c) When all the carbon had been removed and collected in the sinter, it was dried in an oven at 353K for 20 minutes before being stored for analysis.

#### (2) From wood

(a) The blackened surfaces were scraped and the resulting fragments collected.

(b) These fragments were placed in a clean dry centrifuge tube to which Analar Acetone was added.

(c) The sample was placed in an ultrasonic bath for approximately fifteen minutes.

(d) The sample was centrifuged, the solvent decanted and re-used.

(e) The carbon was collected, dried as previously described and stored for analysis.

Before use the pyrolysis wires were cleaned by passing them through the flame of a butane micro-burner. A pyrolysis temperature of 1043K (770°C) for 3 seconds was used for all the experiments, with the probe maintained at 473K.

Prior to the investigation of actual samples reference pyrograms of both TNT and carbon were obtained under the same conditions as used for the samples. Wires were coated with TNT or activated charcoal and pyrolysed.



The samples of carbon to be examined were coated on to the pyrolysis wire by preparing a slurry with distilled water and dipping the cleaned wire into it. It was found that the carbon adhered to the wire after drying so that a sample of about 0.05 mg could be inserted into the probe and pyrolysed.

Initially the mass spectrometer monitored the region of 40–120 atomic mass units (amu) but it soon became evident that the carbon in many cases contained undecomposed TNT, so that the base peak of TNT ( $m/z$  210) could be used for single ion monitoring.

### RESULTS AND DISCUSSION

The mass pyrogram of TNT is shown in Figure 3. The different peaks correspond to surges in the probe internal pressure, and the length of time between pyrolysis and the products reaching the source. The mass spectra corresponding to the peaks a, b and c are shown in Figure 4.

In the analyses of post detonation carbon, TNT itself was found in 20% of the samples examined (out of a total of 40). The pyrogram of a successful run is shown in Figure 5, and the mass spectrum of each peak in Figure 5 is shown in Figure 6. Some material other than TNT is evolved, as can be seen. However, in the unsuccessful analyses no significant ion current was observed at  $m/z$  210. This was also true of the examination of the carbon blanks.

The results obtained in this study were surprising in that it was not expected that TNT itself would be found, rather that decomposition products resulting from the detonation of the explosive would be present within the carbon.

Spectra obtained from the pyrolysis of both TNT and the contaminated carbon differ from the

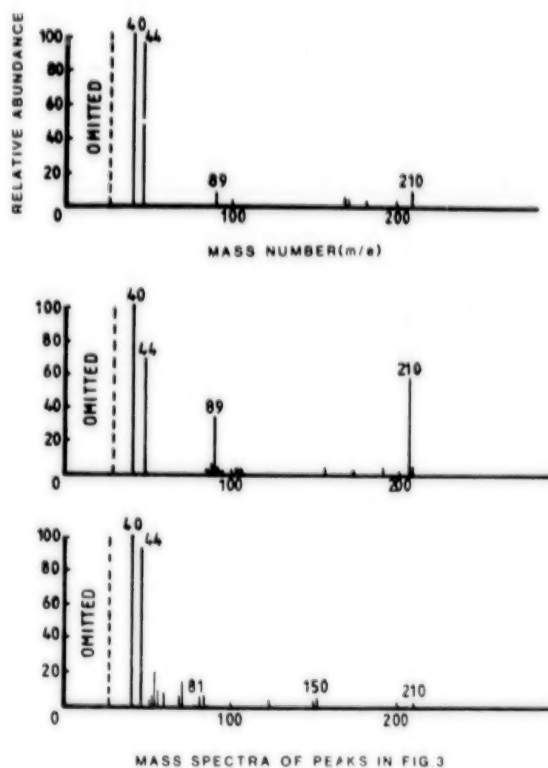


Figure 4 (a)(b)(c)

standard TNT mass spectrum in Figure 7 in one respect: the Molecular Ion at  $m/z$  227 is greatly reduced in intensity if not completely absent. This is probably accounted for by the high energy used in pyrolysing the sample, leaving the molecules in an excited state on entering the source. This would assist the ortho effect in the initial fragmentation of 2,4,6-TNT as described by Bulusu and Axenrod (4). The peak at  $m/z$  210 is the normal 100% or Base peak in the electron impact spec-

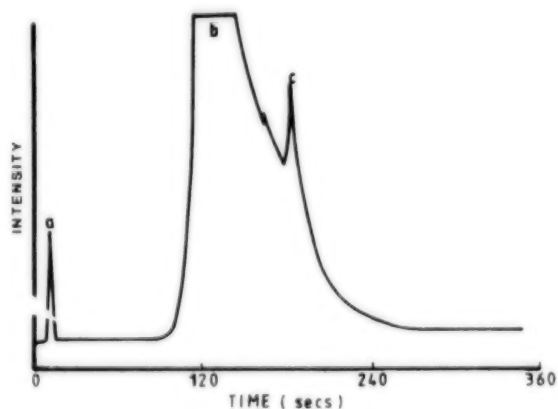


Figure 3 Mass Pyrogram of TNT

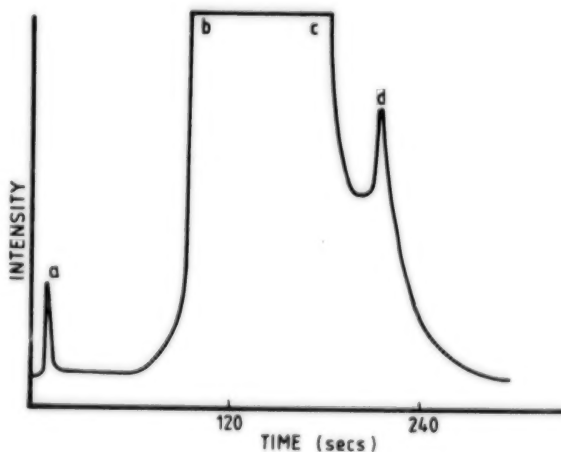


Figure 5 Mass Pyrogram of Successful Analysis

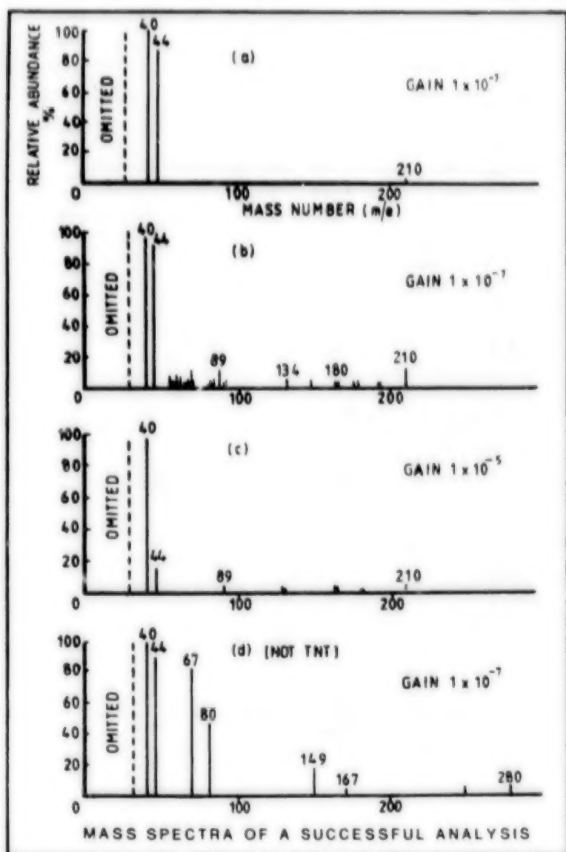


Figure 6 (a)(b)(c)(d)

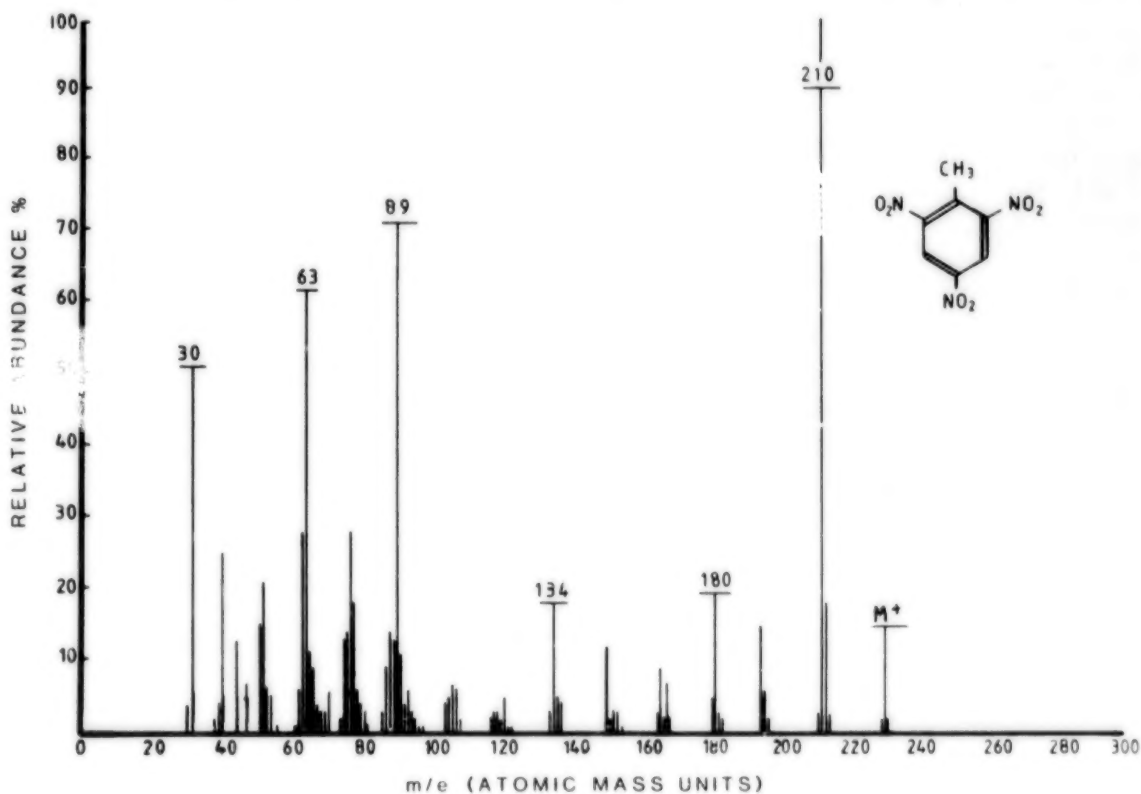


Figure 7

trum of TNT. However, since the same effect is observed for both sample and standard, the absence of the  $M^+$  ion does not affect the identification of the explosive present.

It is difficult to estimate the levels of TNT in the carbon samples since calibration with post-detonation carbon is impossible, and doped samples do not simulate experimental conditions. It has been found that doped samples thermally desorb explosive prior to pyrolysis, but that little or no desorption takes place with test samples. This indicates that the TNT is not merely present as a loosely bound surface layer, but is more firmly attached to the carbon, either strongly adsorbed on active sites on the surface or perhaps trapped within the carbon by means of a process analogous to matrix isolation (5) which would limit the opportunities for further decomposition. This would account for the problems encountered using traditional analytical methods. Its liberation within the pyrolyser must then depend on the rapid expansion of the gases in the carbon when heated by the Curie point wire, causing the carbon to decrepitate and the TNT vapour to escape.

The method described shows great promise for the determination of the presence of TNT in de-

bris. The one in four success rate probably reflects two factors:

(a) The non-uniform dispersal of the TNT in the carbon deposited, leading to high localised concentrations and difficulties in sampling.

(b) Inefficiencies in the removal of carbon from debris, and its subsequent analysis.

Considerable work is being carried out at present on the second factor, principally on modification to the probe to increase its effectiveness.

As supplied, the probe relies on the pressure difference between the sample chamber and the source to draw the pyrolysis products into the mass spectrometer. This arrangement does not permit the use of either Chemical Ionisation or Negative Ion modes, both of which require a significant gas pressure within the mass spectrometer source. There are distinct advantages in using these modes, especially Negative Ion, which is selective for electron capturing materials (6). Therefore a modification to the probe was designed so that a controlled bleed of a gas could be supplied to the base of the pyrolysis chamber and thus provide a 'carrier' to flush released volatiles into the source not only in CI or NI but also in the Electron Impact mode already studied. An additional benefit of this modification is the reduced likelihood of contamination of the probe.

Initial tests indicated that the modification does provide a distinct improvement and that negative ion operation is possible. The identity of the carrier gas appears to be important, the best results being obtained with gases such as hydrogen which may act not merely as a carrier but also as a reagent in the same manner as in the CI mode.

The availability of the negative mode will in-

crease the likelihood of detecting RDX and PETN within post detonation carbon. Both of these materials are much less stable in the mass spectrometer than TNT, and give EI spectra with a base peak of  $m/z$  46. The interferences present in most samples make monitoring of this ion inconclusive in the EI mode. The selectivity of the negative mode should make the identification of residues from both of these possible. A full report on the result of these researches will appear in due course.

## CONCLUSIONS

The technique has the potentiality to become an extremely useful method for the analysis of post detonation residues, not only for traces of TNT but for other carbon depositing materials as well. A great deal of work remains to be done, but it should be possible to devise a routine method of analysis.

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## ON-LINE COMPUTER SEARCH SYSTEM APPLIED TO EXPLOSIVES

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**ABSTRACT.** The analysis of explosive residues by electron impact gas chromatography mass spectrometry and on line computer searching of spectra will be presented. A microprocessor based GC/MS system and related software was used to approach the problem. Real time computer searching of G.C. peaks utilized a pre-selected library of explosive spectra. Methods of sample collection and preparation will be reviewed. For centuries chemists have pondered ways to analyze substances and success would only bring fleeting moments of joy until the chemist was back at the bench trying to improve his methods or yields. At some point in time it becomes necessary to assimilate the research data and implement a simple and reliable method of routine analysis on a regular basis. These methods ideally will be governed by the quality of data, economics of the test and intra-laboratory reproducibility. Our laboratory had access to a small GC/MS which had proven itself quite valuable for drug analysis over the last five years. The instrument is extremely simple to operate and an untrained analyst can usually run a sample by themselves after a few hours training. The down time on our system was about 10%. Data collection, tabulation and library searching was achieved with a microprocessor.

### EQUIPMENT

Equipment consisted of a Hewlett Packard, Model 5992A GC/Mass Spectrometer containing an electron ionization source and quadrupole mass analyzer used to collect standard spectra. The instrument is controlled by a 9825A microprocessor, having a 16K memory.

### SOFTWARE

Software used was Hewlett Packard's On-Line Search Tape, Part #05992-10012, supplied with the instrument. On-Line Search software allows the 5992 GC/MS to perform scanning experiments where a library of up to 50 compounds is searched as each GC peak elutes. The results of the search are printed with the peak height and correlation factor on the chromatogram plot. Operating software and spectral libraries are stored on a single magnetic cartridge.

Background correction is performed automatically. The background taken from the previous valley between peaks is subtracted from the peak

spectrum and the stripped spectra for each peak is saved for later tabulation or search with an off-line library.

The software was modified by our laboratory to accommodate a single library with a capacity of 1,299 pollutants and explosives. The library spectra are stored as the 10 most significant peaks where significance is defined as mass times abundance.

Library entries were added by chromatographing standard explosives and by keyboard entry, using values abstracted from the literature. With experience only about 15-20 masses and their abundances have to be entered for selection of the 10 most significant peaks.

### RESULTS AND DISCUSSION

EI-GC/MS is helpful in identifying some explosives. Data handling capabilities supplied by the microprocessor are adequate for normal qualitative runs. The method of building a library on the ten most significant peaks allows the library to be

stored on smaller space. Searching an unknown, reduced to ten peaks against a library of ten peaks,

is a simple operation on a small computer and could be easily adapted to available equipment.

**Table 1. PROGRAM MODIFICATIONS TO ON LINE SOFTWARE TO LENGTHEN OFF LINE LIBRARY #1 TO 1299 SPECTRA**

From SIM tape or appropriate tape copying program, create a new copy of an "ON-LINE-TAPE" files 0-24.  
 Erase tape copying program ERASE a EXECUTE  
 Locate NULL File (A computer generated file indicating end of valid files)  
 edit 25  
 Mark the remainder of tape for correct file lengths of library segments (13 files of 4000 bytes each, 100 library entries each file)  
 mark 13,4000  
 Allocate space in memory for libraries  
 dim L (550)  
 (L (550) = size of array, derived from each data file being 4000 bytes long and each element of the array being 8 bits long: = there are 4000/8 = 550 elements in each array in each file.)  
 Load data file of desired library in to active memory of computer from original tape, write *PROTECT THIS TAPE AS IN COPYING PROGRAM*.  
 edit N, L (\*)  
 (files 25-28 contain original 400 drug entries; files 29-37 contain original 900 pollutant entries; L (\*) denotes entire data array.)  
 Record data file onto new tape on desired file  
 edit V, L (\*)  
 Repeat for subsequent data files to be moved to make a pollutant library 1299 Spectra long transfer:

FILE	Original Tape		New Tape
29	to		25
30	to		26
31	to		27
32	to		28
33	to		29
34	to		30
37	to		33-37

The above operations will transfer the 517 pollutants held in Library 2 of the 1992 GC/MS ON-Line tape to locations in Library 1 on a copied tape and leave remaining 782 entries available for entry of data of interest. The following operations will adjust parameters used by the system for library searching and modifying.

From Manager *ONCOPIED TAPE* obtain system comments. File 11 contains "GC,MS, and system status save files."

Clear existing program ERASE a EXECUTE

Type

```
dim N (10), V (20), G (10), S (10), R, T EXECUTE
edit 11, N (*), V (*), G (*), S (*), R, T EXECUTE
1299 → V (14) EXECUTE
0 → V (15) EXECUTE
edit 11, N (*), V (*), G (*), S (*), R, T EXECUTE
```

The above allocates space for the arrays defined above, loads them in their entirety, alters some variables (V (14) and V (15)) to allow OFF-LINE Library 1 to be 1299 Spectra long with Library 2 of 0 length. Then re-records this information onto the tape in File 11.

When adding spectra you must replace as opposed to append. The variables controlling the append operation apparently cannot be altered appropriately.

PROGRAMMING BY: Christopher Victor Granger



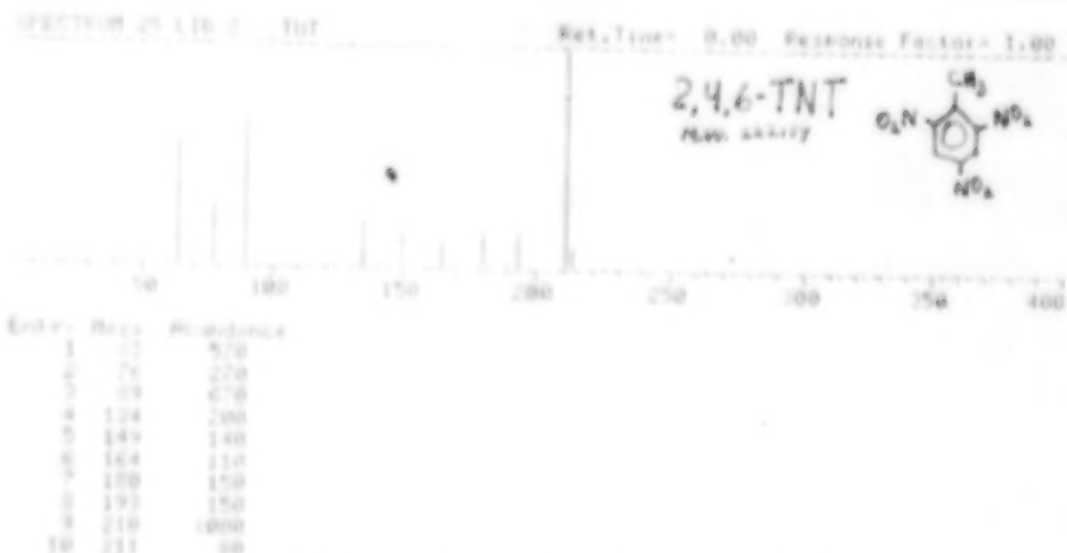
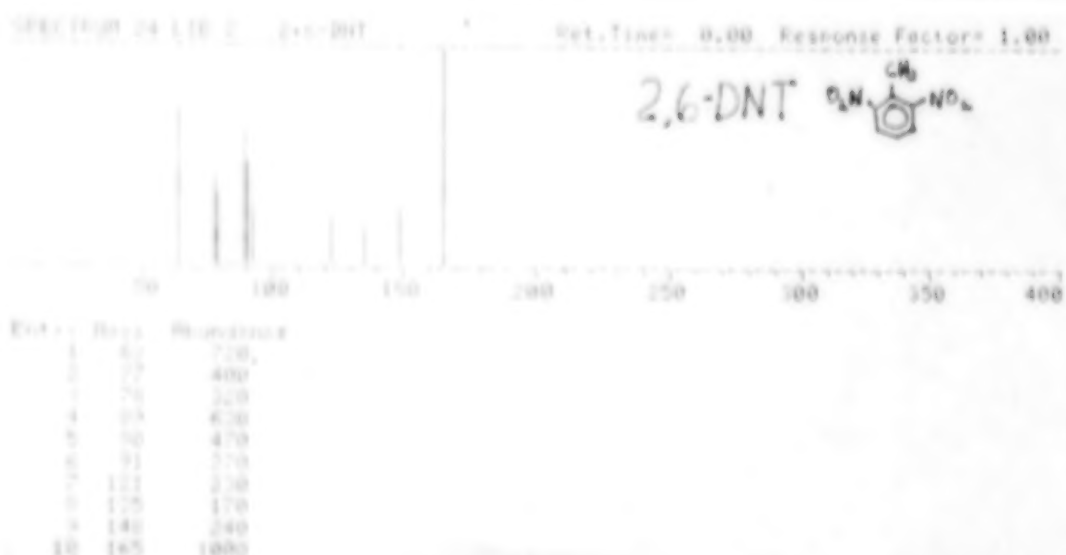


Figure 1. Mass spectrum of three explosives as they appear in the library search program with their ten most significant peaks.

TETRYL (NITRAMINE)

FRN: 3069 LSN: 7 I 6.3 MW 287 C7.H5.N5.O8

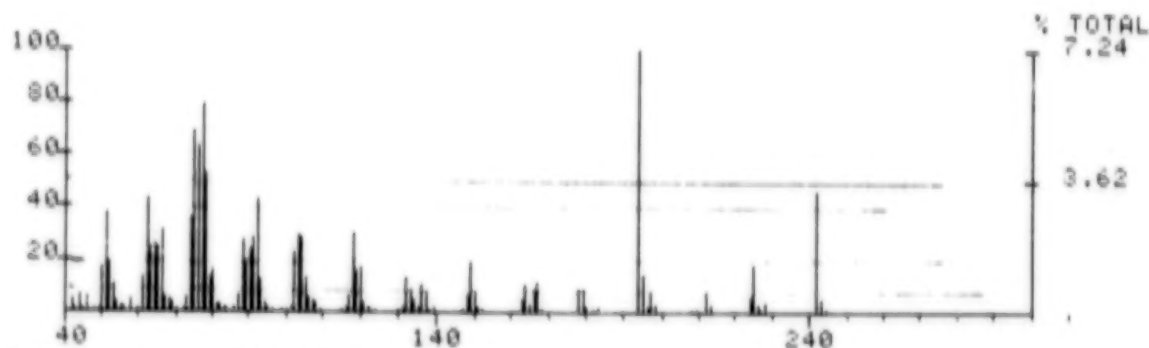


Figure 2. Mass Spectrum of Tetryl from the literature about to be coded. Note reference lines drawn at 40, 20 and 10% abundance.

Off-Line Library Editing Program [rev 10/28/77]

Index	Mass	Abund	Mass*Abundance
1	125	3	375
2	126	25	3150
3	127	100	12700
4	128	18	2304
5	129	18	2322
6	130	3	390
7	173	80	13840
8	174	13	2262
9	175	1	175
10	172	3	516
11	150	14	2100
12	148	14	2072
13	115	70	8050
14	77	20	1540
15	116	12	1392

Molecular Weight = 173.1 Retention Index = 0.00

Entry	Mass	Abundance	Mass*Abundance	Norm. Abund.
1	77	20	1540	200
2	115	70	8050	700
3	126	25	3150	250
4	127	100	12700	1000
5	128	18	2304	180
6	129	18	2322	180
7	148	14	2072	140
8	150	14	2100	140
9	173	80	13840	800
10	174	13	2262	130

Above Spectrum Recorded in Library 1 as entry # 528

Figure 3. Keyboard entry of 1-Mononitronaphthalene and the ten peaks selected by the microprocessor.

## SMOKELESS POWDER IDENTIFICATION

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**ABSTRACT.** Until recently, forensic comparisons of smokeless powders were made based upon physical properties (e.g., size, shape, color) and positive matches would be tentative, especially in the case of burned residues. For the last several years, comparison and identification of both burned and unburned smokeless powder residues have been done in the Federal Bureau of Investigation Laboratory by a combination of physical comparison and chemical analysis using high performance liquid chromatography. Examining both the chemical and physical properties of the smokeless powders allows a more definitive comparison or identification. This presentation will describe a new technique for comparing and identifying smokeless powders based upon the analysis of the trace organic constituents by capillary column GC/MS. The chemical examinations consist of extracting the powder or powder residue with chloroform, and separating and identifying the soluble constituents with a fused silica capillary column GC/MS system equipped with a cold on-column injector. Although this procedure can resolve smokeless powder extracts into as many as 30 major and minor components, only the major components are used for the chemical comparisons. On our GC/MS data system, we have established a smokeless powder "library" (representing about 100 powders) with each entry being a composite spectrum generated by merging the spectra of the major peaks found in the powder extract. Identification of a smokeless powder is effected by computer searching the composite spectrum of the questioned powder against the library. Confirmation of the computer identification is made by comparing the relative amounts of the various components as found by the GC/MS analysis, and by comparison of the physical properties of the known and questioned.

### SMOKELESS POWDER IDENTIFICATION

Smokeless powders are frequently encountered in the Federal Bureau of Investigation Laboratory in connection with improvised explosive devices (IEDs)—both exploded and unexploded. The identification of the smokeless powder or powders

used in the IED is useful for lead purposes and to help characterize the IED and link it to other similar devices. The comparison of smokeless powders is vital when a reloading powder is found in a suspect's possession and a link is sought between the suspect's powder and that used in the IED.

Smokeless powders contain various organic components such as explosives, plasticizers, stabilizers and retarders. The analysis of these volatile organic compounds can assist in the comparison and identification of smokeless powders. Many different procedures are available to compare the constituents of smokeless powders, these include gas chromatography, liquid chromatography, thin-layer chromatography, nuclear magnetic resonance, etc. (Trowell and Philpot (1969), Mach *et al.* (1978), Newlon and Booker (1979), Hardy and Chera (1979) and Meyers and Meyers (1983)).

We have developed a technique which uses injection directly on column, separation on a fused silica capillary column, detection by mass spectrometry and data analysis by computer to compare and identify smokeless powders. A comparison of two smokeless powders is a straightforward peak for peak comparison of the reconstructed total ion chromatograms (TICs) of the two samples' volatile components. The same compounds must be present in the same ratios for two smokeless powders to be considered to have originated from a common source.

The identification of smokeless powders is based on the same comparison technique; however, the TIC of a questioned smokeless powder is compared with the TICs of all previously run known smokeless powders. The actual comparison of a questioned sample against all the known samples which have been run is simplified considerably by using the library search software available on the gas chromatograph/mass spectrometer (GC/MS) data system. We will present data which illustrate the results obtained by using this combination of chromatography hardware and data system software to facilitate these comparisons and identifications.

### MATERIALS

The smokeless powders used in this experiment are all reloading powders. They were obtained directly from the manufacturers over a period of several years.

### EQUIPMENT

The GC/MS used is a Finnigan 4021 quadrupole/mass spectrometer equipped with a Finnigan INCOS 2300 data system. The gas chromatograph was equipped with a Scientific Glass Engineering, Inc., on-column injector and a 20-meter, 0.20 mm ID, SE-54 bonded phase fused silica column. The column was extended through the sep-

arator oven to within several centimeters of the mass spectrometer ionization source.

### EXPERIMENTAL CONDITIONS

Several particles of a smokeless powder (disc, cylinders, ball, flake, etc.) are extracted with 0.5 ml of chloroform for 10 minutes with vortexing. The unconcentrated sample is injected (0.1 to 0.2  $\mu$ l) on-column at ambient temperature outside the gas chromatograph oven. The on-column injector is then introduced into the oven and the oven temperature is programmed at the maximum rate (approximately 20° min) from 70° to 265°. The carrier gas is helium (1 ml/min).

All spectra were obtained under electron impact conditions using the following parameters:

Mass range	45 - 400 AMU
Scan rate	1 sec/scan
Electron energy	70 eV
Filament	0.4 mA
Multiplier	1250 V
Dynode	3000 V
Amplifier	$1 \times 10^{-7}$ A/V
Source press	$1 \times 10^{-7}$ torr
Source temp	350°
Transfer line	250°

### Results

Known samples of smokeless powders are treated as in the experimental section and the resulting TICs are processed with the data system to create a user-generated library of smokeless powders. Processing the data involves summing the mass spectra of all the components of interest and subtracting the contribution due to background. The resulting summed (or composite) spectrum is made a library entry characteristic of the smokeless powder run. This composite spectrum will represent both the volatile organic components and their relative concentrations through the presence and intensities of the ions in the summed spectrum. We have processed approximately 80 different known smokeless powder samples and currently have approximately 150 separate entries in our library of smokeless powders.

A typical smokeless powder (Hercules 2400) will be used as our first example both to illustrate how the library was prepared and how a search of the library is conducted. The TIC of the Hercules sample is shown in Figure 1. The major compounds detected are identified as nitroglycerin, diphenylamine and ethyl centralite. These com-

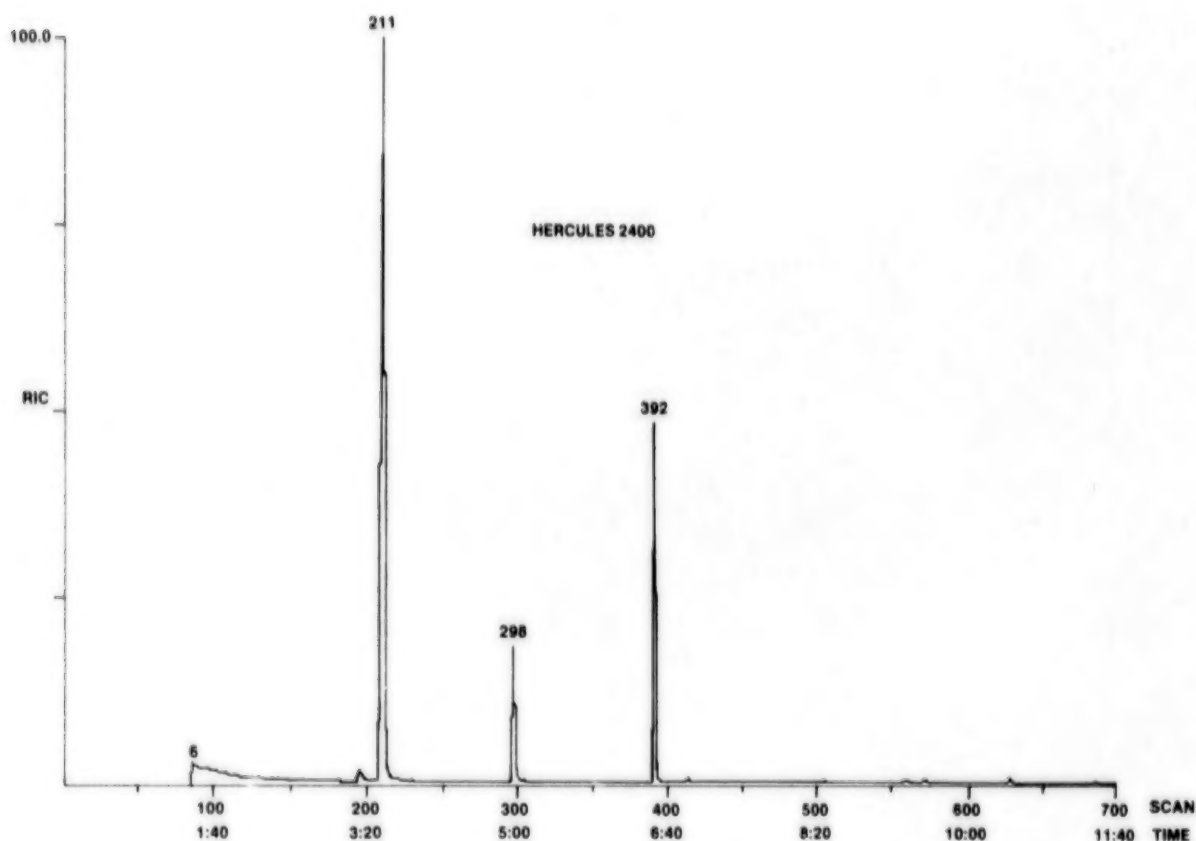


Figure 1. Total Ion Chromatogram of Hercules 2400

pounds were identified by their mass spectra (Figure 2A, 2B, 2C). The spectrum which results from the summation of scans 187 to 413 followed by the background subtraction of the sum of scans 97 to 185 is illustrated in Figure 3. The peak at 46 AMU is from the nitroglycerine and is clearly dominant in this composite spectrum as it is in all double-based smokeless powders. To de-emphasize the nitroglycerine contribution a summation was made from scan 289 to scan 421 followed by background subtraction (Figure 4). This composite spectrum, which omits the nitroglycerine contribution, exhibits major ions due to the diphenylamine and ethyl centralite. These ions were suppressed in the presence of the nitroglycerine ions by the normalization procedure of the data system.

If either of these summed spectra is searched through our library of smokeless powders then a match with Hercules 2400 (Figures 5, 6) results. The library includes entries made using exactly the same technique both with and without the nitroglycerine data. The TICs of all the known samples are also stored by the data system for direct com-

parison with the questioned samples.

Comparison of Norma N-200 smokeless powder (Figure 7) with the Hercules 2400 powder is done as an instructive exercise (Figure 8). It is obvious that the volatile components of the two smokeless powders allow ready differentiation between them using this experimental technique. As usual it is easier to determine that two things are different than it is to determine that they are identical.

The actual identification of an unknown smokeless powder is our goal and when a summed spectrum for the Norma N-200 (Figure 9) is searched through the library the most probable identifications are listed (Figure 10). In this case, as would be expected, the entry for Norma N-200 was listed first. If the sample's origin had been unknown then a comparison of its TIC with the TIC previously obtained for Norma N-200 would be made. A comparison of the TIC of the second best match with that of the Norma N-200 TIC would easily convince the examiner that of all the known samples which have been run, Norma N-200 is the best match.

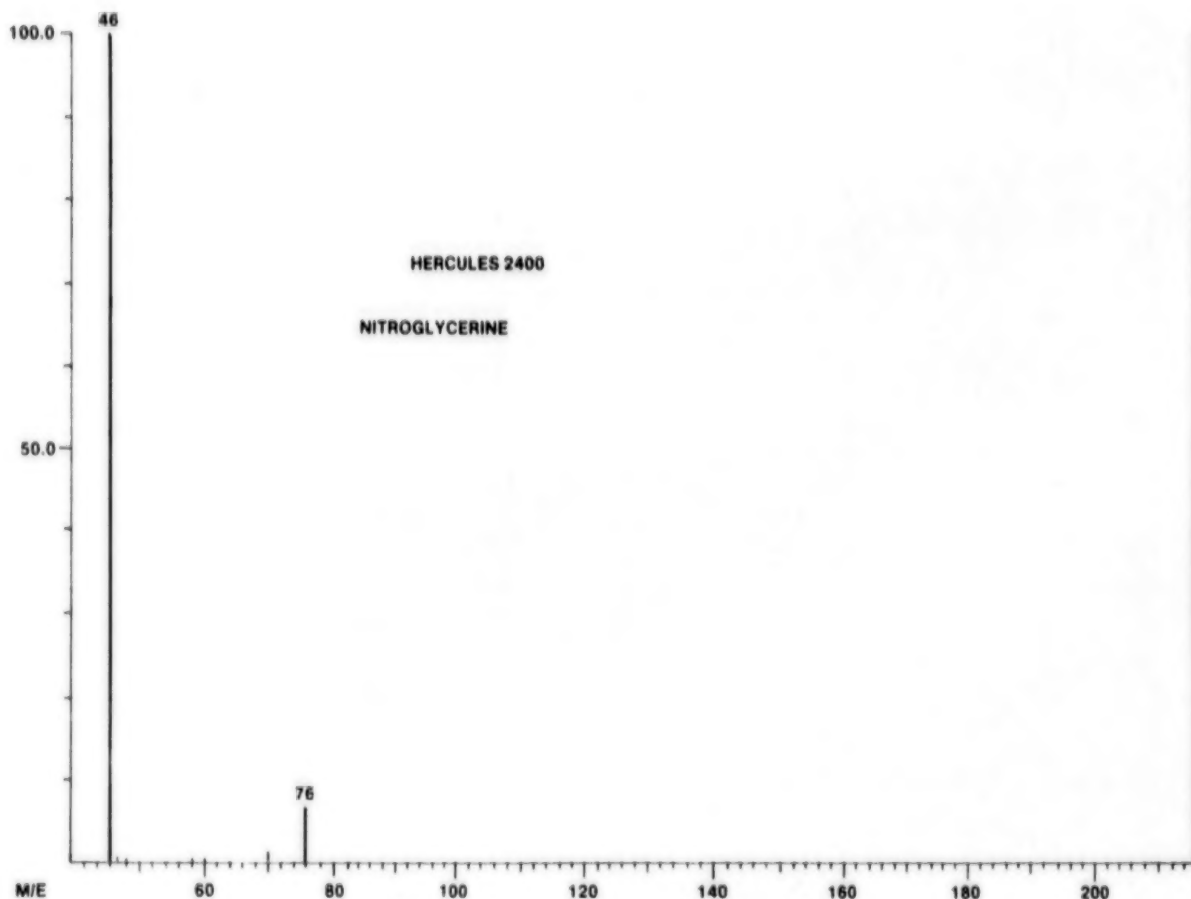


Figure 2a. Mass Spectrum of Scan 211 (Nitroglycerine)

The Norma and Hercules smokeless powders are chemically similar to other smokeless powders in their respective "families" and in some instances to eliminate similar computer matches it is prudent to physically compare the questioned smokeless powder with the known samples to differentiate between close matches. Parameters which can be compared include shapes such as ball, disc or cylinder, as well as dimensions of the various shapes. The data system library search routine allows spectra to be searched under constraints of molecular formula and/or molecular weight range. Our composite spectrum does not have a chemical formula or a molecular weight so these fields can be used to represent the physical shape of the smokeless powder. Letters allowed by the data system including "C", "O" and "N" which normally represent carbon, oxygen and nitrogen in molecular formulas. These letters now represent particles with cylinder, ball and disc shapes respectively. In the Norma N-200 sample the "C" in the area reserved for the molecular

formula in the library search routine denotes a cylindrical particle.

The molecular weight entry in the smokeless powder library is actually a measurement of pertinent dimensions of the various smokeless powder shapes. In the Norma N-200 sample "293" indicates a powder with an outside diameter of 0.029 inches and a length of 0.03 inches. This convention applies to both cylinders and discs. In the case of ball-shaped particles the diameter in thousandths of an inch is entered.

In order to be more specific in our computer searches the shape and dimensions (or range of dimensions) can be specified. This eliminates the need for searching the entire library. The searches in the above examples were done with no restrictions so that the entire library would be searched.

While the emphasis of this paper is on the data system techniques involved, one of the most important pieces of hardware is the on-column injector. This injection system allows the introduction of the smokeless powder extract on to the column



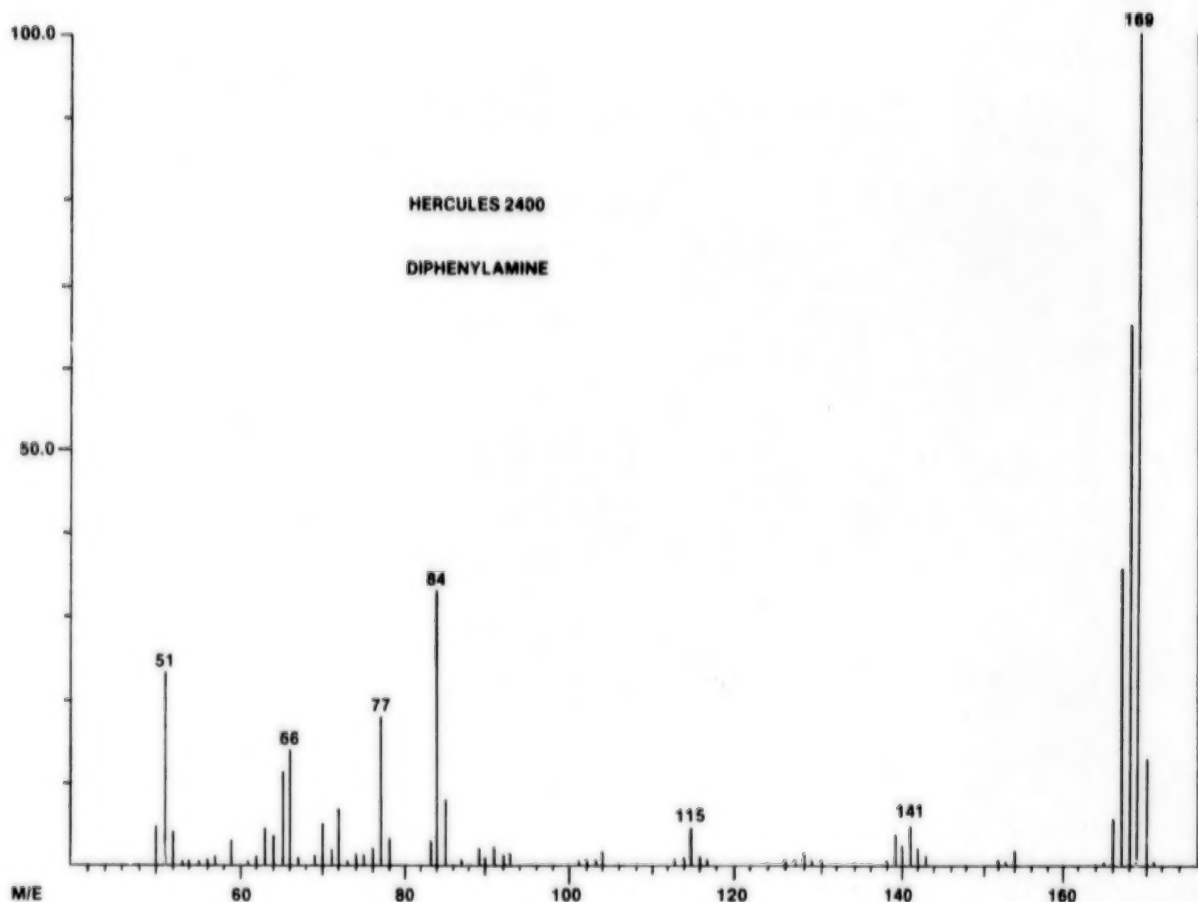


Figure 2b. Mass Spectrum of Scan 298 (Diphenylamine)

with no degradation. In fact the nitroglycerine elutes before the column temperature reaches 100° and is only briefly exposed to elevated temperatures in the separator oven. If a standard injector is used then the injection temperature must be set much lower than normal to avoid decomposition of the nitroglycerine.

An added benefit of the summed spectrum technique is the elimination of any dependence on rigorous reproduction of chromatographic conditions for the tentative identification of smokeless powders. The same summed spectrum will result from a combination of the same components whether the chromatography was performed on a capillary or a packed column. In fact, the use of a packed column with a high injection temperature will result in the decomposition of the nitroglycerine and produce a summed spectrum similar to the summed spectrum using our technique and subtracting the nitroglycerine contribution. The dependence on chromatography for the creation of a summed spectrum could possibly be eliminated

completely by introduction of the smokeless powder extract by solid probe followed by the summation and background subtraction steps.

### SUMMARY

The combination of an on-column injection/fused silica capillary column/mass spectrometer/data system allows rapid identification and comparison of smokeless powders. This technique has already been used successfully to compare residues from fired cartridge cases with smokeless powder deposits found on gunshot victims as well as the more routine cases involving IEDs.

Modification of this technique has numerous possibilities in the identification and comparison of other items of forensic interest which contain mixtures of volatile components or can be pyrolyzed to produce volatile compounds such as paints and fibers. The mode of ionization is independent of the data system techniques involved so chemical ionization and negative chemical ionization tech-

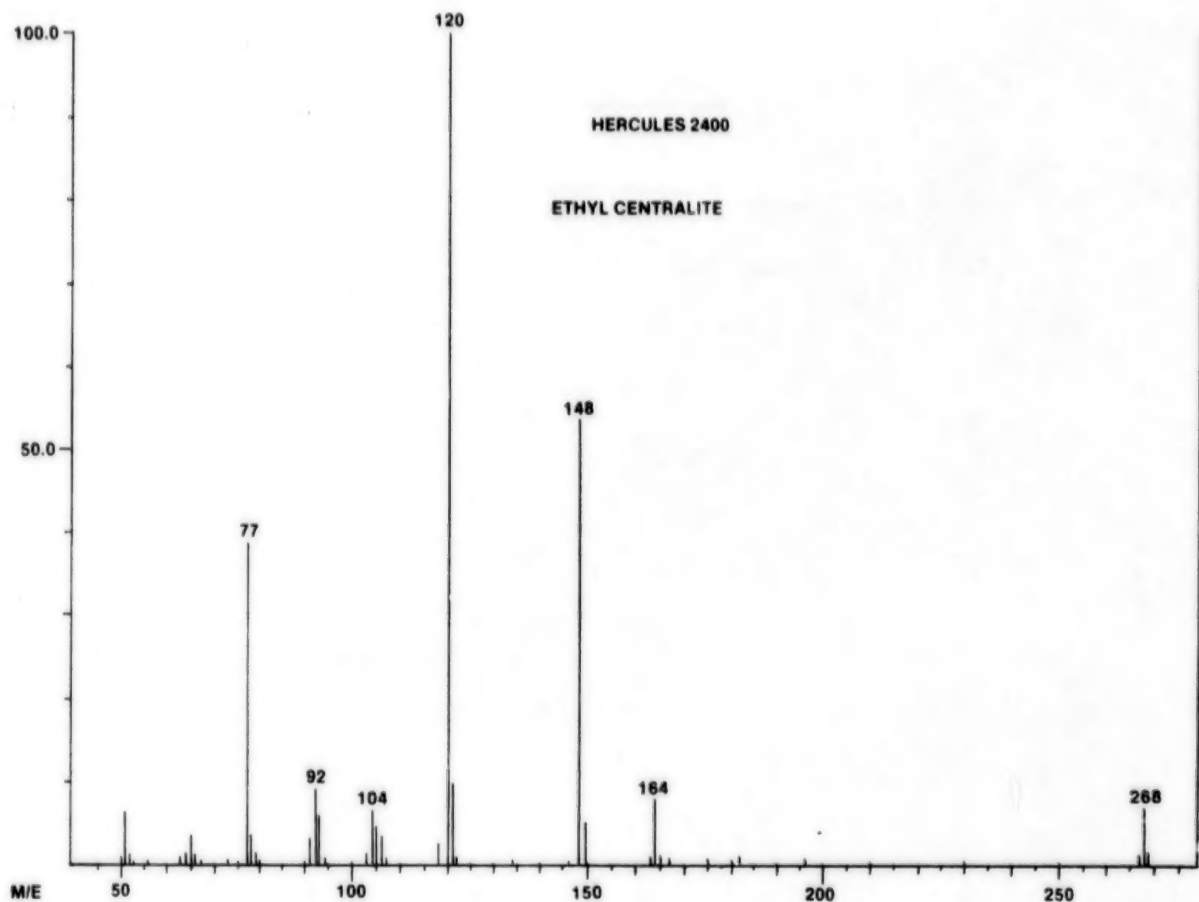


Figure 2c. Mass Spectrum of Scan 392 (Ethyl centralite)

niques may be used to further enhance the specificity or sensitivity of the detection technique.

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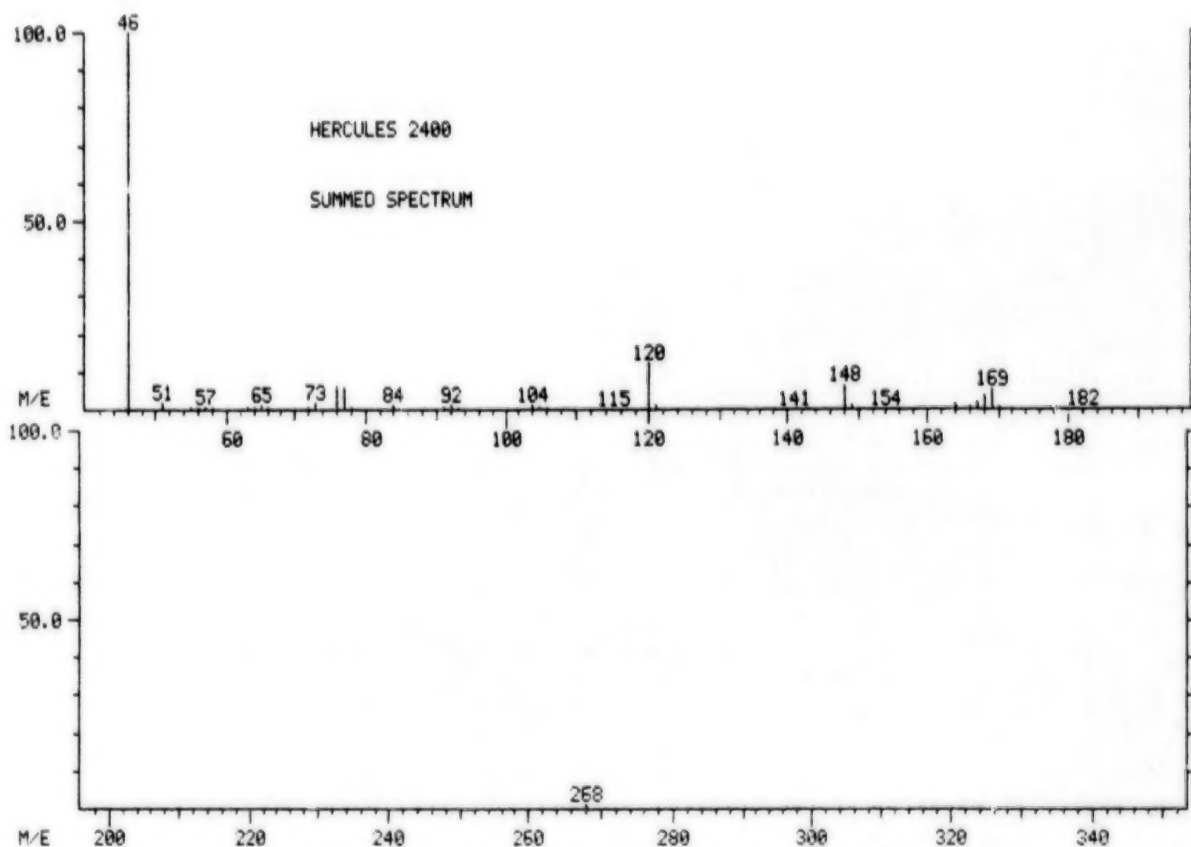


Figure 3. Summed spectrum of Hercules 2400 - smokeless powder

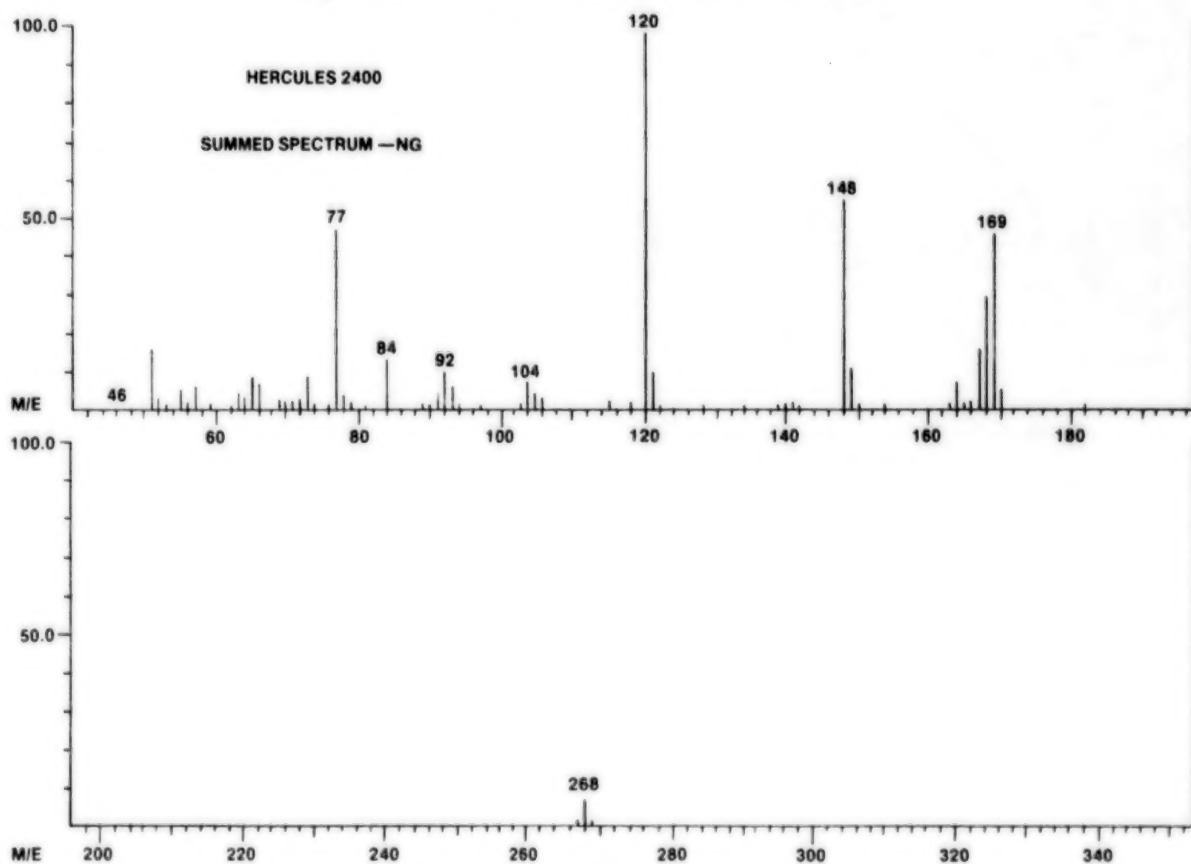


Figure 4. Summed spectrum of Hercules 2400 - smokeless powder - Nitroglycerine

# LIBRARY SEARCH

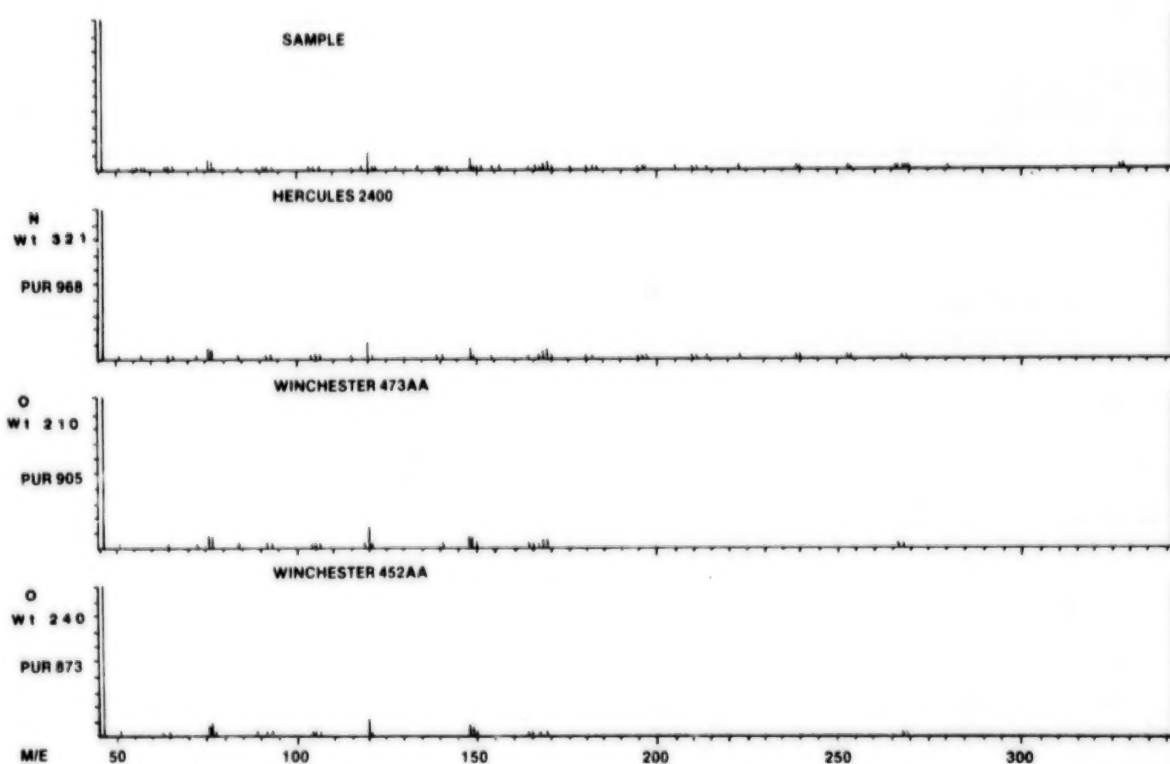


Figure 5. Library Search of the Summed Spectrum of Hercules 2400

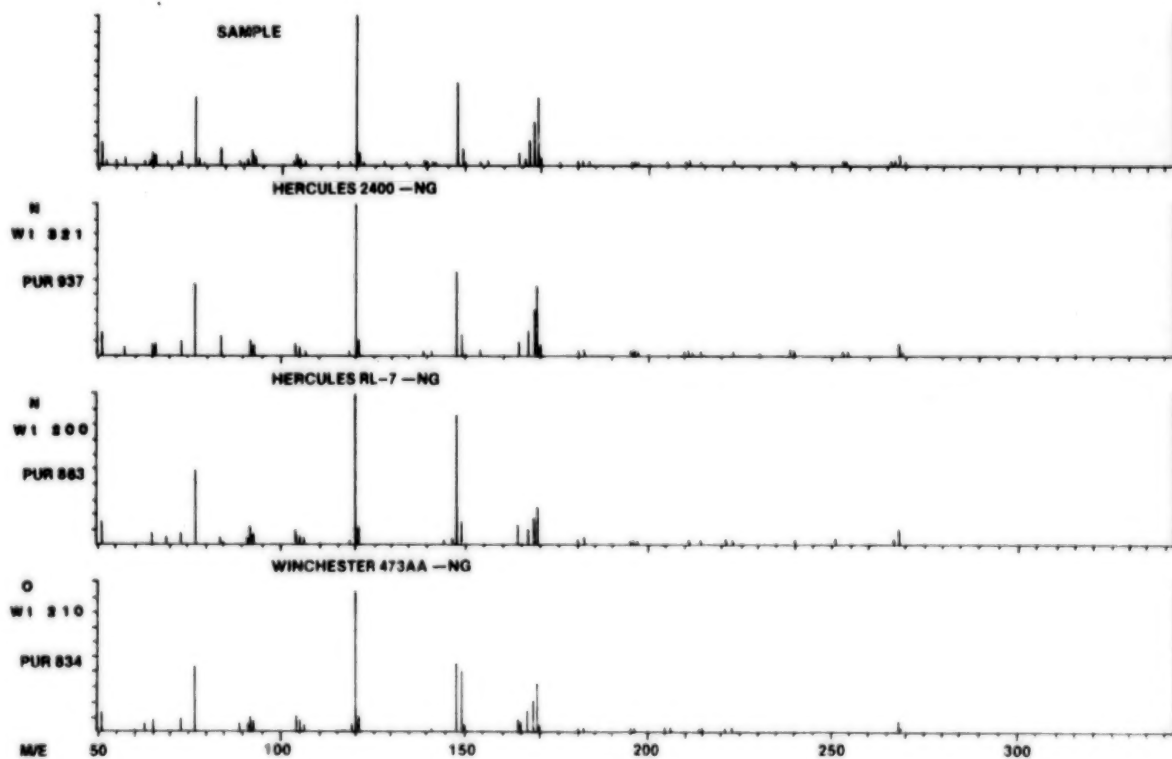


Figure 6. Library Search of the Summed Spectrum of Hercules 2400-Nitroglycerine

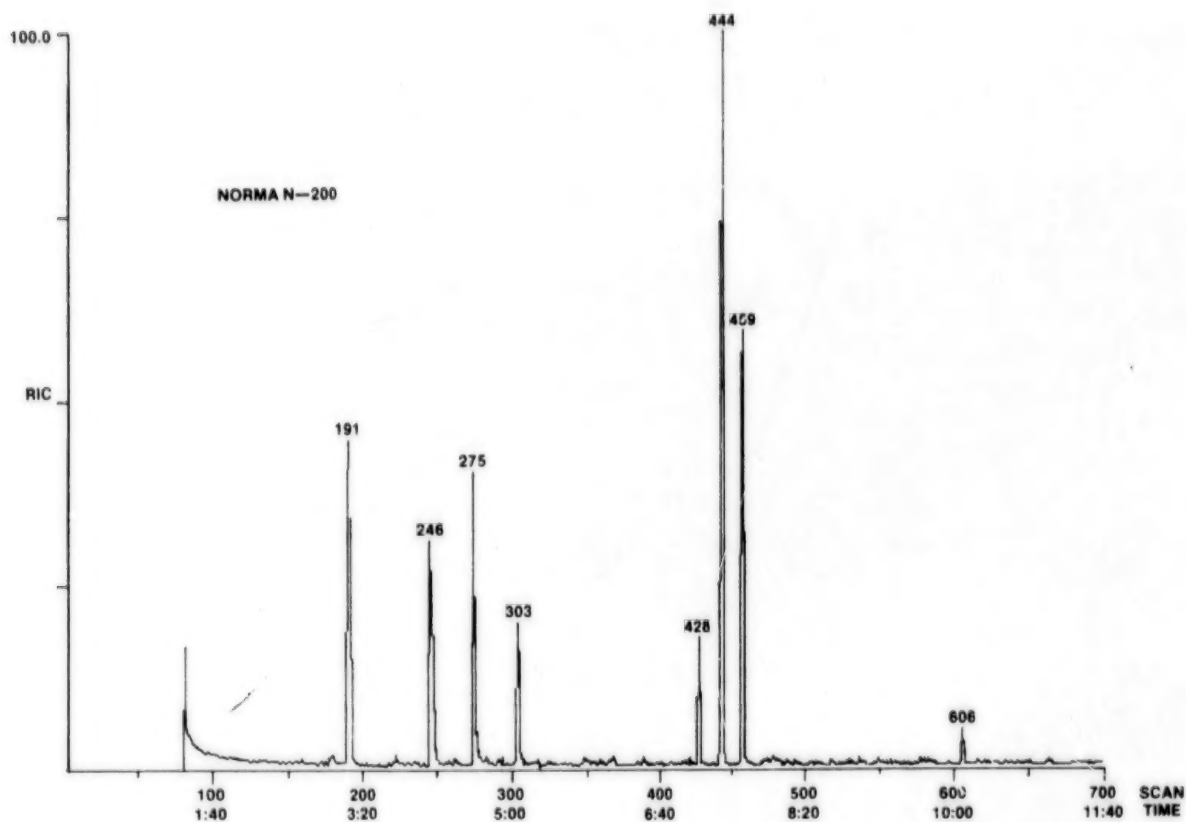


Figure 7. Total ion Chromatogram of Norma N-200

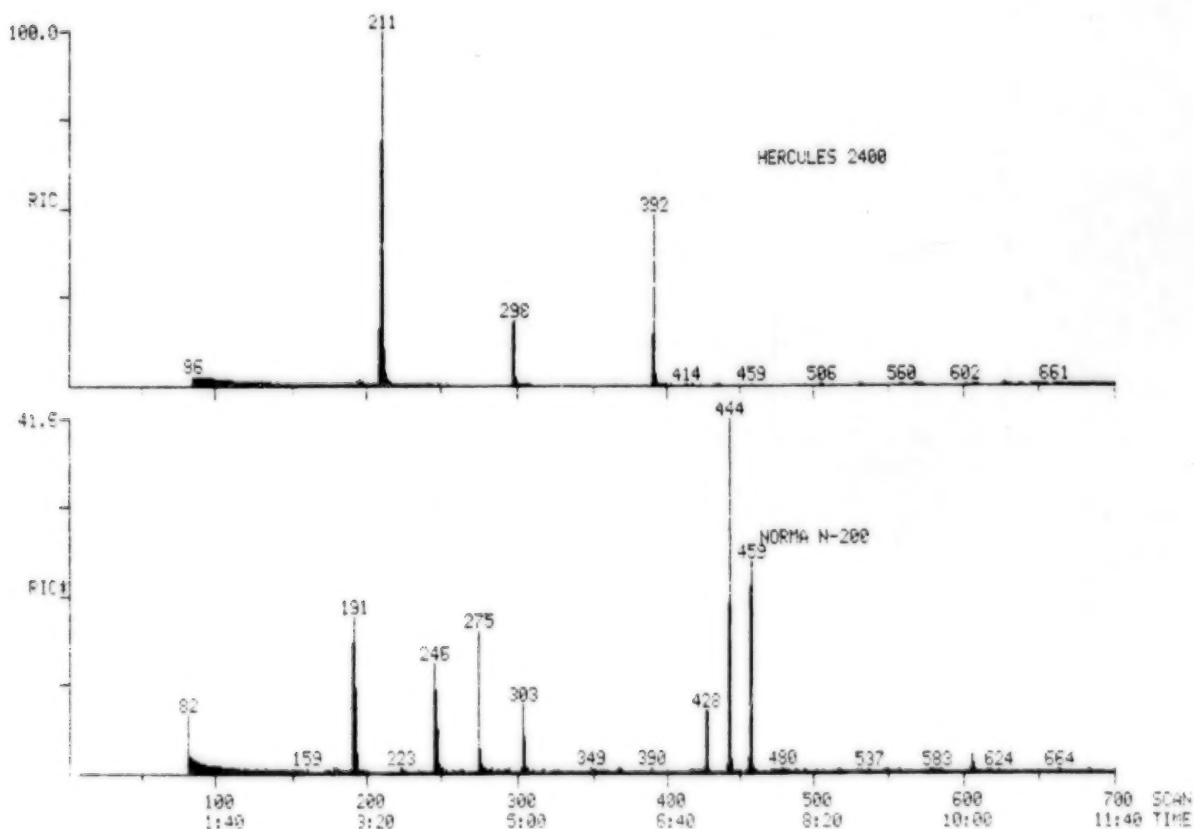


Figure 8. Comparison of the Total ion Chromatograms of Hercules 2400 and Norma N-200

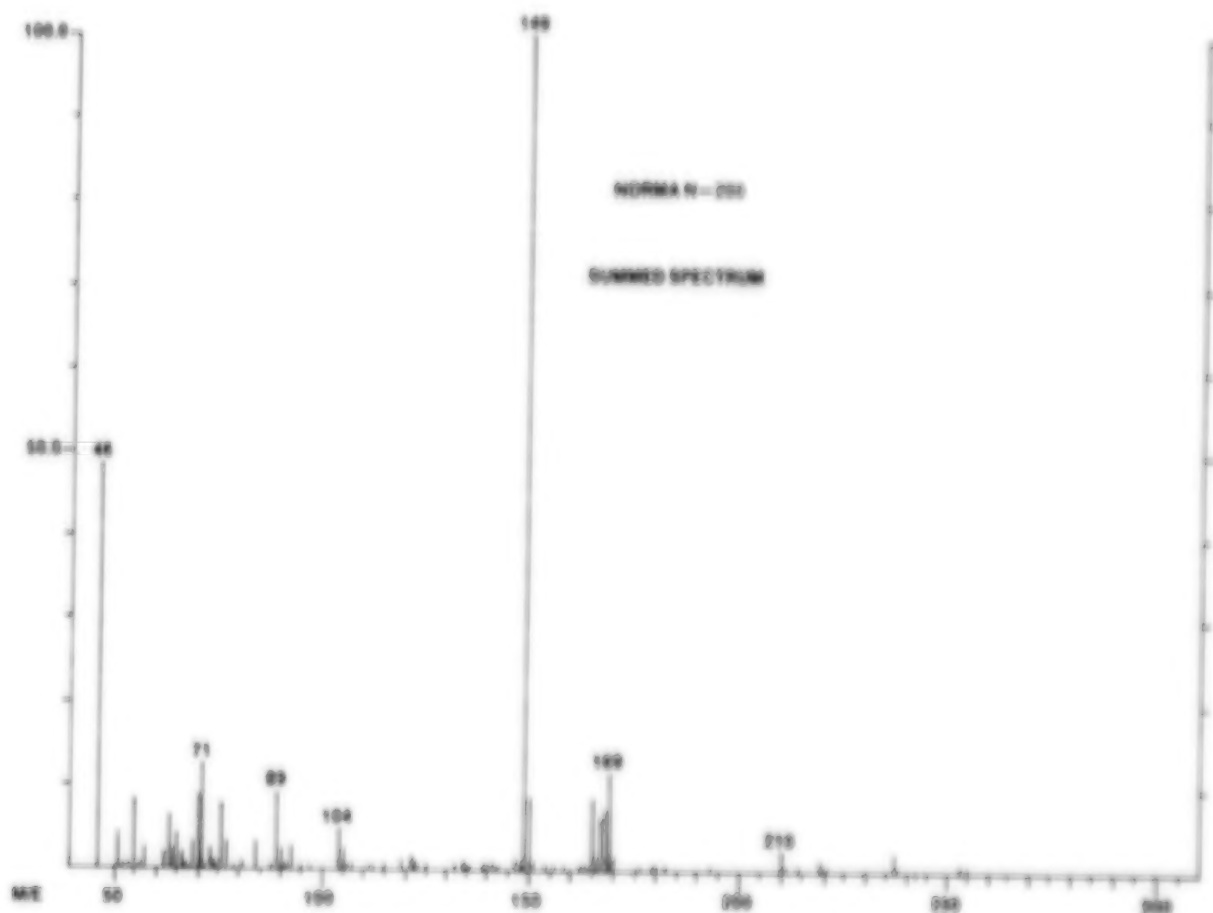


Figure 9. Summed Spectrum of Norma N-200—smokeless powder

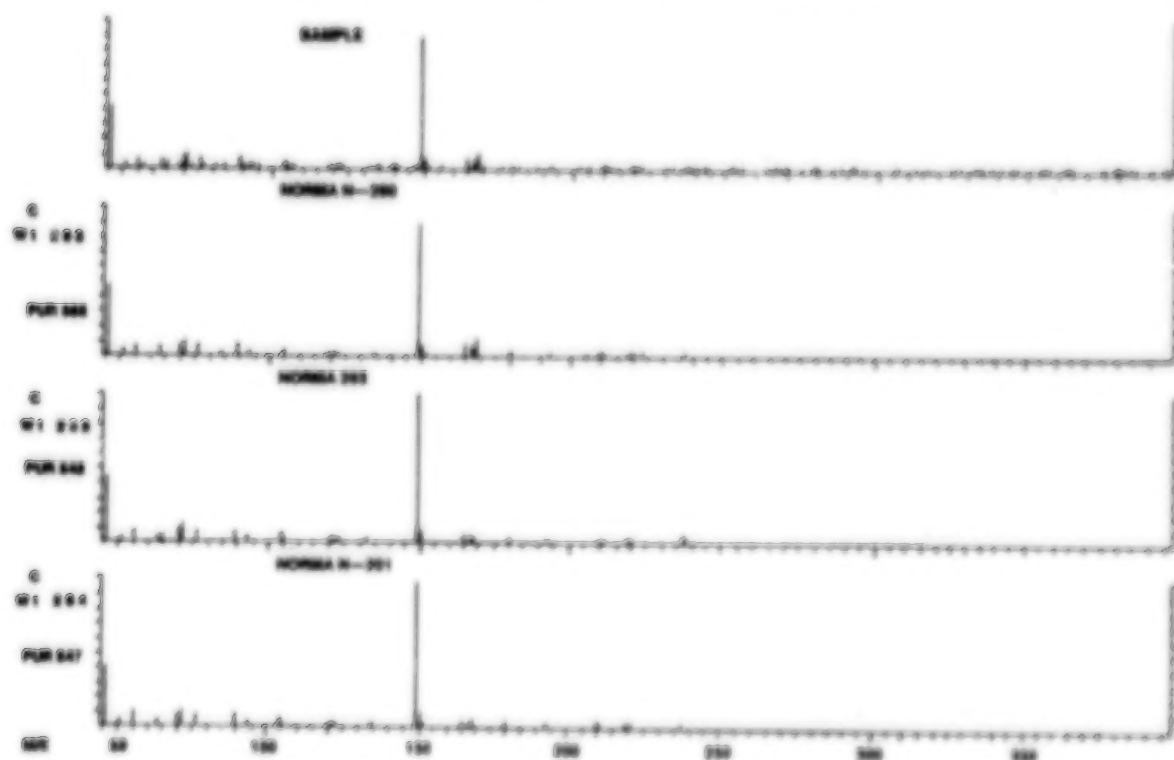


Figure 10. Library Search of the Summed Spectrum of Norma N-200



## FINGERPRINTS OF DETONATION PRODUCTS FROM NAVY EXPLOSIVES

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**ABSTRACT.** The solid products of detonations in nitrogen gas of four Navy explosives have been collected and analyzed. Although graphs of the products do give a rough fingerprint our present examples show too much variation to be of immediate practical use.

### INTRODUCTION

This work was started at the suggestion of Dr. George Young, Naval Surface Weapons Center, Dahlgren, Va., as part of the Navy's Environmental Protection Program. Dr. Young has studied the effect of underwater detonations on marine life and would like to know what damage might be expected from the chemical products of the detonation.

Our initial approach has been to simulate underwater explosions by detonating explosive charges in nitrogen gas. By comparison with similar explosions in air, explosions in nitrogen give much more carbonaceous smoke and lower oxidation state gases. There is also less blast effect in nitrogen. These features correspond to underwater explosions of similar explosives and make our use of nitrogen a reasonable initial approach. Eventually, underwater tests of some charges will be needed to verify the nitrogen work.

The carbonaceous smoke can be collected, extracted with organic solvent and the extract analyzed. This analysis shows several compounds, and our initial work with two explosives, TNT and PBXN-102, showed different patterns of products which conceivably could be used as fingerprints. Our continuing work has shown that we are having trouble repeating a pattern for an explosive from detonation to detonation. We will discuss our experiments and plans for sampling/analysis which we hope will lead to more consistent results for any one explosive.

### EXPERIMENTAL

Our detonations were carried out in a steel walled room with a volume of 38.1 m<sup>3</sup>. The door-

way exits through a labyrinth which has four turns and is about 8 m long. Three openings in the ceiling open into stacks that are 3 m high and 48 cm in diameter. A steel baffle plate 1 m in diameter and 7 cm thick protects fans in each of the stacks. For our nitrogen tests, the doorway and stacks are closed with plywood and polyethylene sheeting. Liquid nitrogen is pumped into the room—570 liters of liquid nitrogen lowers the oxygen content below 1% (which is satisfactory judging from  $\alpha$  or results). Unfortunately, the liquid nitrogen also cools the walls which may cause condensation of part of the product vapors. The explosive charge is placed in a Dewar flask to maintain it at ambient temperature. We have detonated the explosive shown in Table I.

Table I. EXPLOSIVES DETONATED

TNT C <sub>7</sub> H <sub>5</sub> (CH <sub>2</sub> ) <sub>2</sub> NO <sub>2</sub> <sub>3</sub>
Pressed with density = 1.602 g/cm <sup>3</sup>
PBXN-102
HMX
Al
Polymer

Charges of about 1,000 g are detonated with a 30 g booster so that the ratio of products will strongly favor the main charge. Our gas sampling sequence is started just before the detonation so that we can measure the amount of oxygen in the room atmosphere before the explosion. After the detonation, the doorway and ceiling vents are open so we have only a short time (30 sec) to collect samples.

The sampling system has been described in a technical paper by J. H. Johnson, E. D. Erick-

son, S. R. Smith, and C. A. Heller. *Products From The Detonation of Trinitrotoluene In Air And Nitrogen*. Naval Weapons Center Technical Publication 6420, Nov. 1983. It consists of two 1/2-inch outer diameter stainless steel tubes going through the wall of the room about 75 cm above the floor. Gas and particles from the room are pumped through both lines and through a filter to protect the pump. From these main lines, samples can be taken through side lines into evacuated flasks or small filters of Tenax, charcoal, Porapak, or other adsorbents.

To date, the solids analyses have been done by extraction of filters with pentane. A new technique for thermally desorbing small  $\text{C}_{10}$  directly into the gas chromatograph (GC) should make our analysis quicker. The GC peaks are analyzed using a Hewlett Packard Model 5985 GC/MS.

The gas in the flasks is sampled via a T tube with a septum on one arm going into a gas syringe and then into a GC which has a thermal conductivity detector. These samples are described by Johnson *et al.* in his technical paper.

## RESULTS

Detonations of TNT in air and in nitrogen emit very different smoke patterns. Air produces a small amount of white smoke while nitrogen produces a heavy black smoke. Detonations with oxygen varying from 21% down to 0.5% showed a sigmoid shaped curve of oxidation of the gaseous products. At 21% oxygen,  $\text{CO}_2$  was the only product found in the gas samples (water was not measured).  $\text{CO}_2$  begins to decrease when there is about 15% oxygen and at about 5% oxygen reaches a constant value while at the same time a small amount of hydrocarbon and a trace of hydrogen appears. This lack of change below 5% oxygen leads us to think we need not reach 0% oxygen to simulate underwater conditions.

We picture the water explosions to be that of an underwater bubble as a fairly self contained gas with only small interaction with the water at the interface (Figure 1). The gas stays at a high concentration and cools slowly. In an ambient temperature gas, the hot gas mixes rapidly with the cool gas. This is shown by the fact that in air all the C is oxidized to  $\text{CO}_2$ . However, the concentration of intermediates such as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2$  must remain high enough, even in nitrogen, to allow for the formation of methane, ethylene and carbonaceous particles by bimolecular collisions. An underwater bubble might be expected to provide a



Figure 1. Concept of Detonation Underwater and in Air in Nitrogen.

more uniform reaction volume and therefore give a more uniform product pattern than does the diffusion mixture in nitrogen.

Our product patterns from TNT and PBXN-102 are shown in the Figures 2-5. We show only the larger peaks and have used an arbitrary decision about what the cutoff should be. Not even the same list of products shows in patterns from the same explosive.

One consistency is that unreacted TNT appears with the products from TNT detonations. RDX and PETN do not appear with their products. TNT even appears from detonations in air. This is consistent with the large amount of TNT which comes out with the black smoke from burning TNT.

## DISCUSSION

The hypothesis that the products of a detonation reaction will depend upon the explosive requires a little discussion (McGuire, 1979). If the

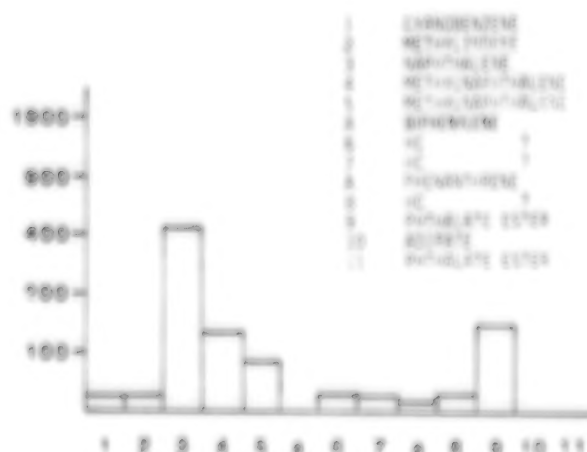


Figure 2. Detonation Products from PBXN-102 in Nitrogen on Quartz Wall (43).

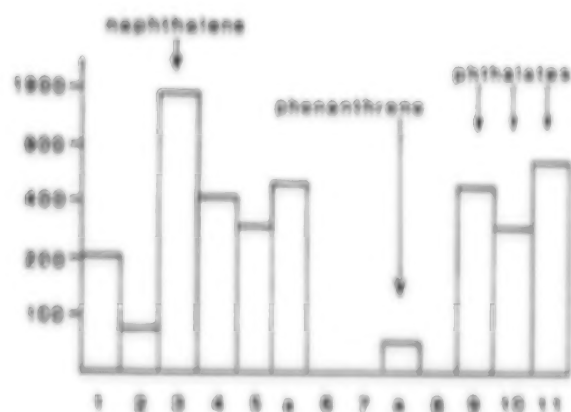


Figure 3. Detonation Products from PRXN-102 in Nitrogen on Texas (E41). Product Numbers are the Same as Listed in Figure 2.

explosive breaks down to atoms which then reassemble to molecules and carbonaceous particles, the products would depend upon the atomic composition, temperature, pressure. Then, any two explosives with the same atomic composition and



Figure 4. Detonation Products of Pressed TNT in Nitrogen on Texas (E36).

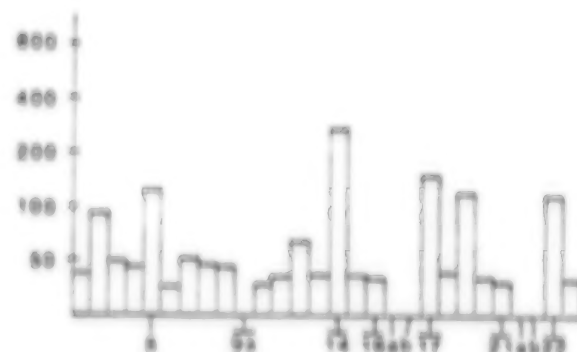


Figure 5. Detonation Products of Pressed TNT in Nitrogen on Texas (E39). Component Numbers are the Same as Those Listed in Figure 4.

equal energy would give intermediate atomic mixes which would then combine to give the same fingerprint of the product. That is, a given product fingerprint could come from different original explosives.

A more likely picture would be that a portion of the molecules don't break down to atoms in the detonation, but retain some of their structure. Then, the recombination of atoms and atomic groups might give rise to a few large molecules whose composition would depend upon the original explosive's molecular composition. These large molecules would be found condensed on the carbonaceous particles on chamber walls or in water for an underwater detonation. The discovery of unreacted TNT in our experiments shows that large "fragments" can survive detonations under some conditions. Others at this conference (Sharma, 1983) have reported similar findings including monomolecular coatings on pipe bomb casings. On the other hand, one would expect fewer molecular remnants for confined explosives than for our unconfined tests.

Real underwater detonations of confined explosives should form a good test of the atomic recombination hypothesis. The original confined molecules might be expected to break down completely to atoms. Then, the underwater bubble would form a uniform, reproducible reaction chamber where atoms could recombine to form a pattern of molecules.

To date, our work has proven nothing about product fingerprints. We have shown that some molecules survive the detonation. We have found some large molecules we think are from the explosive. Our sampling system has needed improvements and these are being made. We shall continue to study how much carbonaceous product is

formed and how large a burden of toxic chemicals are carried on these particles. However, we will also examine the fingerprints as we continue.

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## THE ANALYSIS OF TRACE LEVELS OF EXPLOSIVE BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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**ABSTRACT.** The identification of trace levels of explosive is a problem faced by forensic analysis. In principle the Mass Spectrometer is a very powerful tool for use in these analyses, since considerable structural information can be obtained from the mass spectrum. However, when dealing with explosives in a conventional Mass Spectrometer major problems are experienced due to the extensive fragmentation, particularly with the non-aromatic nitrate esters and nitrocompounds such as nitroglycerine and RDX. Much use can, however, be made of this limited information by the use of a high efficiency capillary Gas Chromatograph coupled to the Mass Spectrometer. Some of the problems will be described and the detection limits possible with Single Ion Monitoring of the most abundant ion (typically in the low nanogram range) will be discussed. Other forms of ionisation are possible, however, and the application of the negative ion mode will be described. This technique is particularly appropriate to the analysis of explosives, since electron capture is the principal mechanism of ionisation, and common explosives are strongly electron capturing, a property made use of in their Gas Chromatographic analysis. Not only does the negative ion mode produce improved detection limits, but also introduces a degree of discrimination not available in conventional Mass Spectrometry. The implications of these newer developments in Mass Spectrometry for the analysis of explosives traces will be discussed.

### INTRODUCTION

Mass Spectrometry is generally considered to be one of the most powerful tools available to the analytical chemist for the characterisation of an unknown material. A review of its application within the field of explosives analysis has appeared (1). However, the analysis of explosives by conventional mass spectrometry presents problems. Ionisation by electron impact (EI), in which the sample is bombarded by electrons at 70eV in high vacuum, produces substantial fragmentation of most explosive molecules and hence oversimplified spectra whose usefulness as a means of identification is limited.

This limited usefulness arises from the poor charge stabilising properties of the nitro group. Molecular ions of nitro-alkanes eject the nitro group so readily that a molecular ion ( $M^+$ ) is seldom observed. Under the standard EI condition

of 70eV and high vacuum none of the nitrate esters gives a molecular ion. The major peaks which occur at 30, 46 and 76 mass units are due to fragments identified as:



In contrast aromatic nitro compounds do give molecular ion peaks and are thus more amenable to study in EI. The fragmentation of TNT has been studied in detail (11) and it has been shown that the Base Peak at  $m/z$  210 corresponds to  $(C_7H_4N_3O_2)^+$  which corresponds to the loss of OH from the molecular ion.

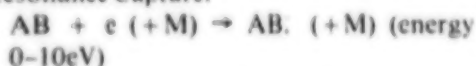
In order to make the best possible use of this limited means of characterisation, it is essential to achieve an efficient separation of mixtures prior to ionisation. This is commonly done by attaching a Gas Chromatograph to the Mass Spectrometer (GC/MS). The method may be employed with packed, borosilicate capillary or fused silica capil-

lary columns. Fortunately most of the explosives regularly encountered are sufficiently volatile to be amenable to gas chromatographic analysis.

Although EI mass spectrometry has been the standard technique for many years, mass spectrometry is applicable to both positive and negative ions. Because of the greater ease with which reproducible EI spectra may be obtained from most molecules the study of negative ion spectra has been neglected until recently (2,3). The revived interest is due to improvements in both ionisation techniques and instrumentation, allowing machines designed primarily for positive ion operation to be easily adapted to produce and detect negative ions.

For an explosives analyst the attraction of negative ion (NI) spectrometry lies in its selectivity. Under appropriate conditions the predominating mechanism of ion production is electron capture, behaving in the same fashion as the gas chromatographic electron capture detector, one of the most sensitive explosives detectors available. It has been shown that the spectra depend on a large number of variables (2,3,4), e.g. temperature, pressure, ionisation energy. The three distinct mechanisms by which negative ions can be formed, each of which is dependent on electron energy are:

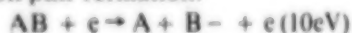
(a) Resonance Capture.



(b) Dissociative resonance capture.



(c) Ion pair formation.



where AB is the species under examination; e is an electron, and M is a moderator species.

Due to the low energy required to produce resonance capture the presence of a moderator or buffer gas (M) is necessary to maximise the process in a conventional mass spectrometer source. A pressure of approximately 1.33 kPa is required. This moderator, usually a gas such as methane or nitrogen enhances the formation of low energy electrons (0-10eV) which are then captured by the sample. At low pressures the other two mechanisms (b and c) predominate. These are intrinsically inefficient methods for the production of negative ions giving rise to radical or positive ionic spectra and extensive fragmentation.

At high pressure (2.66-3.99 kPa) fragmentation can be practically eliminated, producing spectra analogous to those observed under positive ion chemical ionisation conditions (CI). At these pres-

ures additional reactions take place within the ion source (1).

The work described here was undertaken to investigate the sensitivity of the VG 16F in positive and negative mode as a means of identifying traces of explosive. It was thought that a combination of the two techniques would prove of considerable use in GC/MS analyses. Low pressure NI-MS using methane as a moderator was studied as it was considered that acquiring the additional information from fragmentation of the sample molecules would be an advantage. High pressure NI-CI mass spectrometry was not studied at this stage. Recently, however, some reports of its application to the analysis of nitrate esters within the biochemical field have appeared (5,6,7). These studies indicate the high sensitivities possible, with picogram detection limits reported.

## EXPERIMENTAL

All mass spectra were obtained on a VG Organic 16F single focussing magnetic sector instrument. The schematic layout is shown in Figure 1. It is equipped with packed and capillary column gas chromatographic inlets. The packed column inlet is equipped with a jet separator to remove excess carrier gas.

The mass spectrometer has been modified using a set of standard units supplied by VG Analytical to enable negative ion spectra to be obtained. This equipment enables the polarity of the accelerating voltage and the ion beam focussing controls to be reversed (-4kV to +4kV). The polarity of the electromagnet was also reversed, but the electron multiplier was maintained at -2kV, the momentum of the ions in the flight tube being sufficient to overcome the deceleration produced.

For the study of negative ion spectra methane was introduced into the source via an inlet system

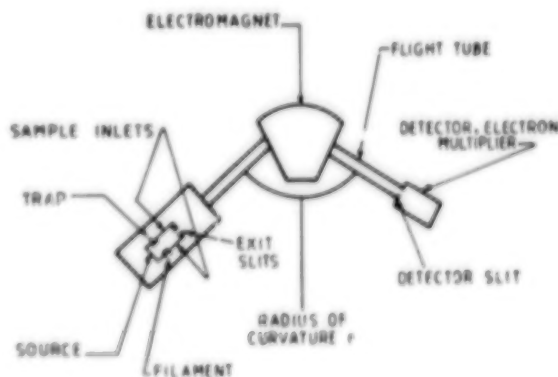


Figure 1. Schematic Layout of a Mass Spectrometer



controlled by pressure equalisation valves, thus ensuring a steady supply of gas to the source. This system was designed for use in chemical ionisation studies but is equally applicable to negative ion work. A pressure in the source housing of  $2.66 \times 10^{-3}$  kPa was used giving an approximate pressure of 0.6–2 kPa within the partially sealed source.

The source conditions used for both positive and negative ion studies are respectively Emission current, 200 and 500  $\mu$ A; Electron Energy, 70eV for both.

The chromatographic materials used were:

Packed column 2m 3% OV17 on Chromosorb W(HP) 80–100 mesh. Flow 20 ml  $\text{min}^{-1}$  He.

Borosilicate Capillary 12.5 m  $\times$  0.5 mm id. WCOT OV17. Flow between 1 & 3 ml  $\text{min}^{-1}$  He.

Fused Silica Capillary. 12.5 m  $\times$  0.2 mm id. Methyl Silicone. Flow rate approx 1 ml  $\text{min}^{-1}$  He.

The samples used were obtained from pure reference collections and are listed below:

Ethylene glycol dinitrate: EGDN

Nitroglycerine: NG

Tetramethoxymethane tetranitrate: PETN

1,3,5-trinitro-1,3,5-triazacyclohexane: RDX

2,4,6-trinitrotoluene: TNT

Single Ion Monitoring (SIM) of the most abundant ion was used to determine the detection limit.

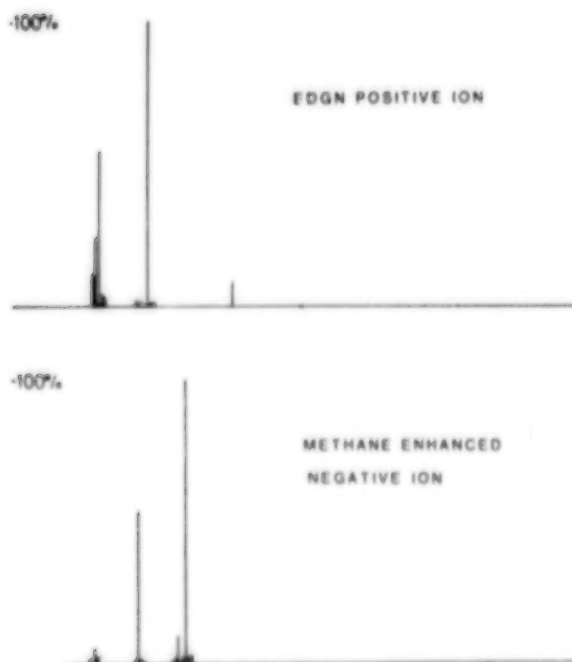


Figure 2

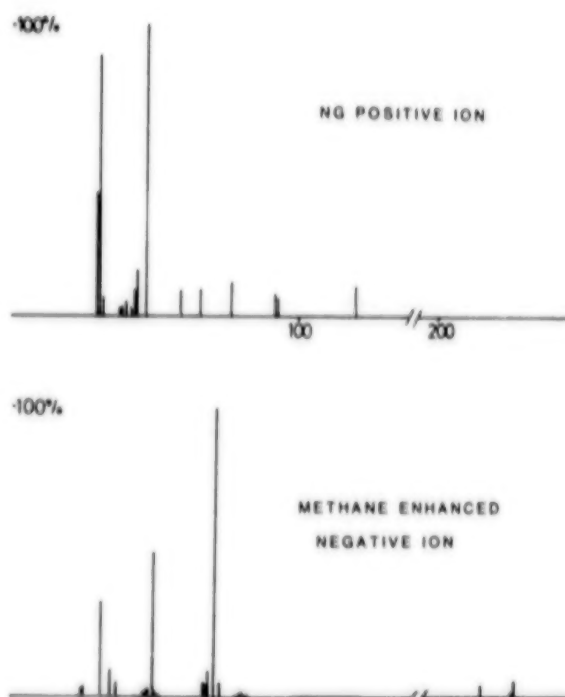


Figure 3

Prior to attempting GC sensitivity experiments samples of pure explosives were examined to obtain reference spectra. The positive and negative ion spectra are shown in Figures 2–6.

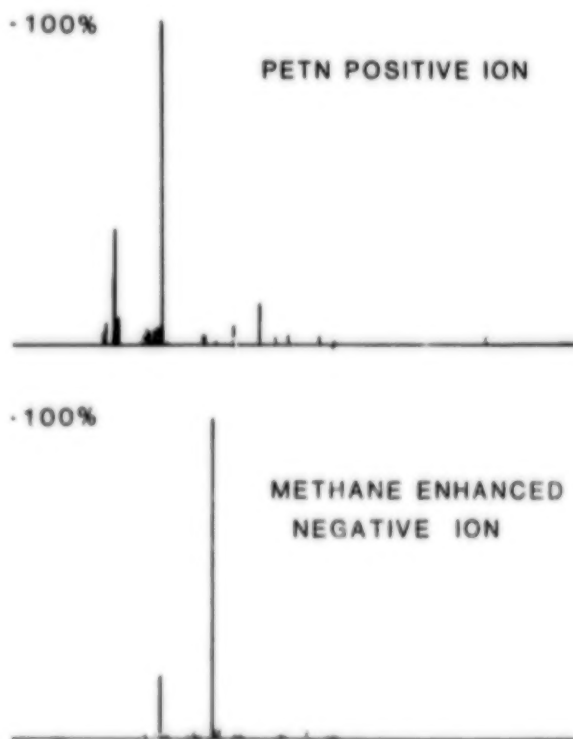


Figure 4

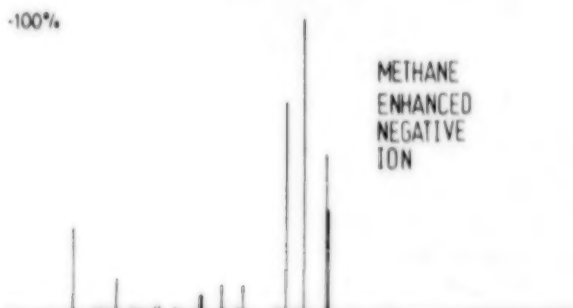
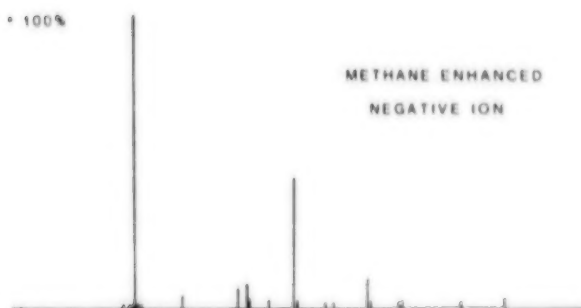
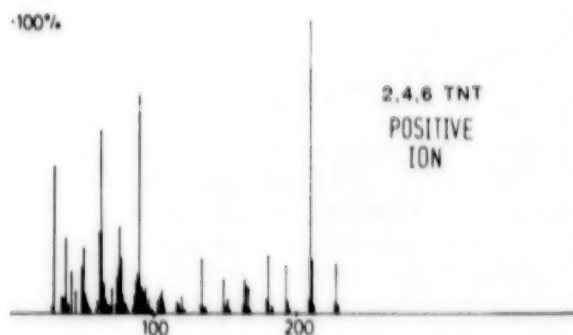
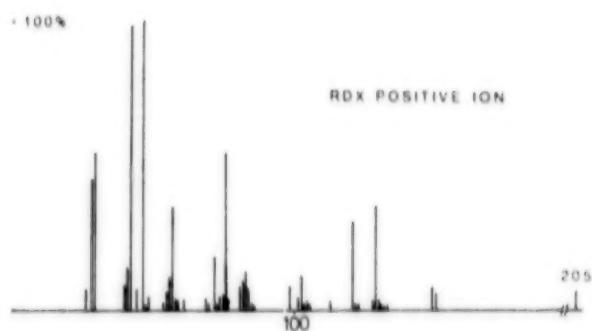


Figure 5

Figure 6

A standard sample volume of 0.2  $\mu$ l was used for all capillary work, and splitless injection was employed, thus allowing direct injection of small amounts.

The sensitivity to a given explosive depends on the percentage of the total sample which is present in the mass spectrum as the ion whose intensity is being monitored. Molecules which are totally ionised to give a single species, whether a molecular ion or not will give a better detection limit than molecules which undergo extensive fragmentation. With most of the explosives examined the second situation is experimentally observed, and

thus the sensitivity is lowered. Because the fragment at  $m/z = 210$  is relative stable, TNT undergoes less complete fragmentation and this contributes to its low detection limit compared with that of NG.

It is apparent that the overall sensitivity of the spectrometer is far greater using capillary columns than with the packed column, and that fused silica columns offer an increase in sensitivity over borosilicate columns. The reasons for this are various. The 60–70% efficiency of the jet separator essential for packed column operation accounts for some loss in sensitivity, but more important are

## RESULTS AND DISCUSSION

### Detection Limits for Positive Ion Operation.

Explosive	Sim Ion	Packed Column	Borosilicate Capillary	Fused Silica Capillary
EGDN	46	100 ng	1 ng	250 pg
NG	46	100 ng	10 ng	1 ng
PETN	46	100 ng	25 ng	10 ng
RDX	46	500 ng	200 ng	30 ng
TNT	210	5 ng	520 pg	50 pg

### Capillary Chromatographic Conditions for Positive Ion.

Explosive	Manifold Temp ( $^{\circ}$ C)	Injector Temp ( $^{\circ}$ C)	Oven Temp ( $^{\circ}$ C)	Source Temp ( $^{\circ}$ C)
EGDN	150	125	90–165*	150
NG	150	125	90–165*	150
PETN	150	125	90–165*	150
RDX	200	200	200	200
TNT	250	250	210	200

\*TEMPERATURE PROGRAM—Initial Temp: 1 min; Temp Ramp:  $3^{\circ}$ C min $^{-1}$ ; Final Temp 10 mins.

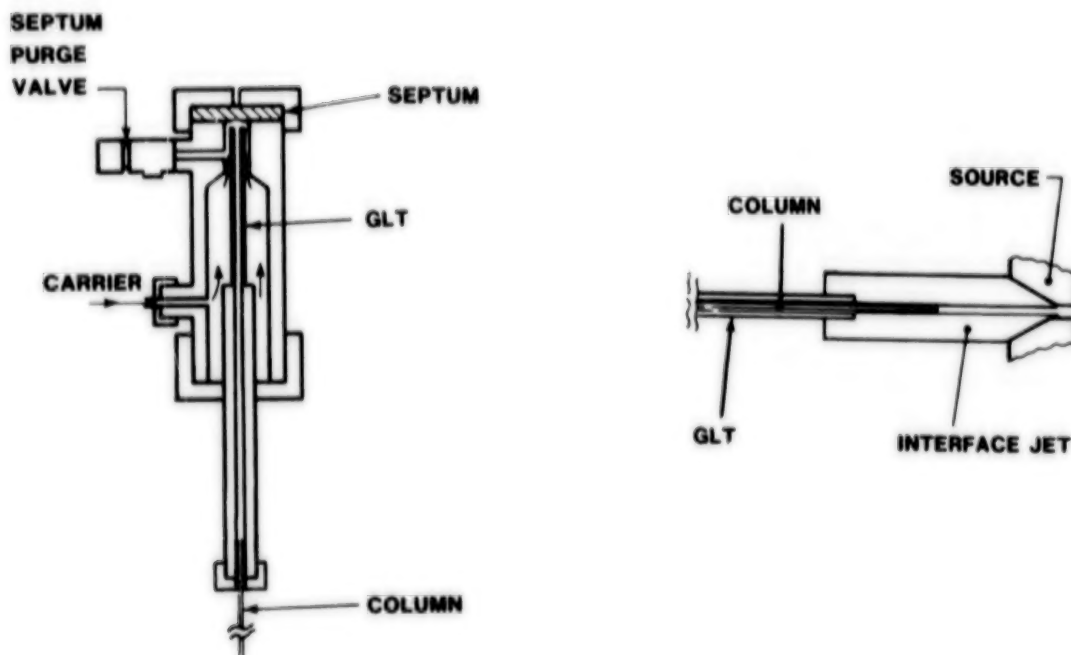


Figure 7

the opportunities for sample loss within the column. This may be minimised by the use of all glass equipment since nitrate esters in particular readily decompose in contact with hot metal. This decomposition may be further reduced by removing all active sites. Due to impurities within most common glasses a substantial number of these active sites are present on the accessible surfaces of both the packed and borosilicate capillary columns. Fused silica contains far fewer active sites of this kind and therefore the detection limit for susceptible materials is lower. In addition the flexibility of the fused silica column permits direct connection

to the mass spectrometer source, avoiding the use of lengths of connecting tubing, (Figure 7).

Experience has shown that the performance of fused silica columns does tend to deteriorate with time, probably due to column bleed rendering active sites on the column wall accessible. This effect should be minimised by using bonded phases, the application of which is currently under evaluation.

The detection limits for negative ion GC/MS of explosives were determined solely with fused silica capillary columns, because of the greater sensitivity achieved with them in EI mode. The limits obtained are shown below.

#### DETECTION LIMITS FOR NEGATIVE ION GC/MS OF EXPLOSIVES.

Explosive	Sim Ion	Detection Limit
EGDN	62	250 pg
NG	62	1 ng
PETN	62	10 ng
RDX	46	30 ng
TNT	210	125 pg

#### GC Conditions for Negative Ion GC/MS.

Explosive	Manifold Temp (°C)	Injector Temp (°C)	Oven Temp (°C)	Source Temp (°C)
EGDN	150	150	100	160
NG	150	150	145	160
PETN	150	150	155	180
RDX	200	250	190	200
TNT	250	250	230	200

It is clear that NI-MS is likely to have a major impact on the use of mass spectrometry in the detection and identification of traces of explosives. In operation the ionisation processes are compara-

ble to those in the Electron Capture Detector which has become essential in the GC analysis of explosives for reasons of both sensitivity and selectivity. This means that it is possible to operate

at high sensitivity in the presence of considerable amounts of non-electron capturing solvent. Solvent creates a major problem in EI where solvent tails can prevent confirmation of the presence of explosives. Similarly the presence of non-electron capturing impurities in the sample will cause far fewer problems than can be experienced in EI.

The spectra themselves are relatively simple, and provide evidence additional to that furnished by EI. Under the conditions produced by a low pressure of moderator gas there is often insufficient evidence to characterise the explosive using NI-MS alone. However, the combination of NI, EI and a GC retention time provides very strong evidence indeed for identifying the species. For example in the case of NG: SIM at 46 mass units in NI and EI; SIM at 62 mass units in NI and a retention time corresponding to that of NG indicates the presence of an electron capturing compound containing species which give rise to (a)  $\text{NO}_2^-$  (46); (b)  $\text{NO}_2^+$  (46); (c)  $\text{NO}_3^-$  (62). Apart from nitrobenzene (NB) (Figure 8), only nitrate esters give rise to appreciable amounts of  $\text{NO}_3^-$ , and NB can be eliminated by a study of the ratio of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  which is close to 2 for nitrate esters and close to 0.5 for nitrobenzene. In addition the molecular ion peak for nitrobenzene is approximately the same intensity as the  $\text{NO}_2^-$  peak. These two factors provide enough information to eliminate NB. Therefore using the SIM information it is possible to identify a nitrate ester by comparing its retention time with that of a known standard, e.g. NG. This gives very convincing evidence of identity. Further evidence would depend on the sample amount, since below a level generally an order of magnitude greater than the detection limit, it is impossible to obtain a complete spectrum. The work carried out so far indicates that the detection limits obtainable in practice for NI are of the same order as for EI. This is not as good as might be expected, since it has been suggested that sensitivities at least an order of magnitude greater should be obtainable for NI (Reference 8). The explanation for this probably lies in the compromises made in modifying the 16F to obtain negative ion spectra. A dedicated instrument would be capable of a much closer approach to the theoretical sensitivities. In addition the conditions used for this study may not be optimum. The pressure of moderator gas employed may not be producing the optimum mean free path for negative ion production, and this together with a 2kV deceleration at the collec-

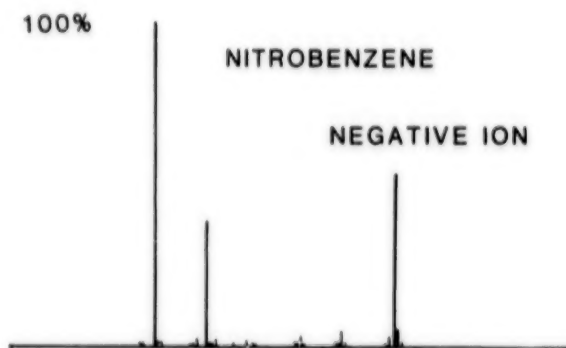


Figure 8

tor will drastically lower the efficiency of the system. Some further work on moderator gas pressure will be necessary to resolve this point. It is worth noting that the spectra of explosives obtained with methane differ somewhat from those obtained in nearly identical conditions with isobutane (Reference 9).

Methane at the pressure employed does not prevent fragmentation of the molecular ion. In order to increase the sensitivity and indeed the selectivity, this fragmentation should be minimised, which would result in a greater intensity of the molecular ion. However, fragmentation can be useful in providing additional evidence of the identity of the sample, e.g. distinguishing the DNT isomers. It has been reported that chlorinated species, such as  $\text{CHCl}_3$  enhance the molecular ion by the formation of ion clusters (Reference 10). It may be possible to approach the suggested sensitivity of NI by making use of gases such as  $\text{CHCl}_3$  and  $\text{NH}_3$  in the low pressure mode. This may stabilise the molecular ion to some extent, though full stabilisation is not likely without operating at high pressure, i.e. NI-Cl. Further work will be undertaken to confirm whether this behaviour is observable with the present instrument. The fragmentation observed with methane as the moderator is not identical to that observed in EI. As yet the routes are not well documented. But a notable feature is the formation of  $\text{NO}_3^-$  (62 mass units) as the base peak in the nitrate esters, EGDN, NG and PETN. Since, apart from NB, the other nitrocompounds studied do not give this ion, and since NB is readily distinguishable, this provides a means of identifying nitrate esters. Both nitrocompounds and nitrate esters give  $\text{NO}_2^-$  (46 mass units). As  $\text{NO}_2^-$  this forms the base peak observed in EI for nitrate esters and non-aromatic nitrocompounds.

The detection limit of TNT in the negative mode

is somewhat higher than in EI. The use of 210 mass units for SIM for both NI and EI detection limits means that the sensitivity depends on the proportion of the total ion current that reaches the collector as the ion of mass 210. The negative ion spectrum of TNT has a much enhanced molecular ion  $M^-$  with a corresponding decrease in the sensitivity when 210 mass units (which remains the base peak) is used for single ion monitoring. The base peak of 210 indicates that the loss of  $OH^-$  is still a major feature of the fragmentation of TNT, but that the molecular ion is much more stable.

Further fragmentation in TNT does take place, but apart from a major peak at 197 mass units, assigned as  $C_7H_5N_2O_5^-$  (Reference 1), which also takes an appreciable proportion of the total ion current, it is at a low level. This pattern of fragmentation suggests that under the correct conditions the fragmentation could be completely eliminated, leading to the use of 227 for single ion monitoring and greatly enhanced sensitivity.

The identity of the various fragment ions remains to be determined for most of the explosives studied. Such identification would require considerable work, including accurate mass determinations and possible isotopic substitution. However, the lack of such data does not preclude the use of NI as an analytical method of great value and of negative ion spectra as a 'fingerprint' characteristic of a compound.

### CONCLUSIONS

The combination of EI, NI, and high performance capillary chromatography provides a very powerful analytical system capable of giving a

clear positive identification of explosives material at minimum levels between 100–150 ng, depending on the explosive, at which levels a complete mass spectrum may be obtained. Using Single Ion or Multiple Ion Monitoring of the most abundant peaks a very high degree of confidence of identification is possible at picogram levels.

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# ANALYSIS OF EXPLOSIVES AND EXPLOSIVE RESIDUES WITH ION MOBILITY SPECTROMETRY (IMS)

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**Abstract.** The detection and analysis of explosives using Ion Mobility Spectrometry (IMS) is described. Results for trinitrotoluene (TNT), dynamite, cyclonite (RDX), and composition B (TNT/RDX) are presented. Methods by which sample can be introduced into IMS are discussed. These include ambient air carrier gas, sample wire probe/syringe, solids probe, desorption oven, membrane inlet, exponential dilution flask, standards generator, surface sampler, and gas chromatography. A compact IMS system is described which has obvious application as an explosive vapor detector.

## INTRODUCTION

A problem of significant interest to forensic science is the detection of explosives and explosive residues either before or after a detonation incident. A variety of techniques have been considered for this application including high pressure liquid chromatography, thin layer paper chromatography, gas chromatography using electron capture or photoionization detectors, ion chromatography, mass spectrometry,  $\text{NO}_x$  chemiluminescence, light microscopy and X-ray photoelectron spectroscopy. This paper describes another technique known as Ion Mobility Spectrometry (IMS). With proper sampling techniques, IMS can be used to analyze and detect explosives in the vapor, liquid or solid phase with basic sensitivities approaching one part in  $10^{11}$  or 1 picogram (Spangler and Lawless 1978, Karasek 1974). Because IMS works under atmospheric pressure conditions, it avoids excessive hardware encountered with vacuum technology and can be miniaturized into a compact detector alarm system for field use (Carrico, *et al.* 1982).

## ION MOBILITY SPECTROMETRY

### The Technique

Figure 1 illustrates the technique of IMS. IMS consists of a cell in which there exists two regions: (1) the reaction region and (2) the drift region. In the reaction region, a carrier gas flows

whose composition is typically purified air (i.e. air with less than parts per million of water and less than parts per billion of ammonia,  $\text{NO}_x$ , and halogenated compounds). A Ni-63 radioactive source ionizes the carrier gas to produce what are called reactant ions. When sample is introduced into the carrier gas, the reactant ions undergo ion/molecule reactions with the sample to produce product ions. Under the influence of an electric field, the mixture of ions are drawn to a shutter grid where they are introduced into the drift region. The shutter grid is pulsed "on" and "off" periodically to introduce small amounts of ions into the drift region.

Once in the drift region, an electric field draws the ions to a collector (Faraday Plate) where they are collected as pulses of ion current separated by arrival times of ions. These pulses are amplified by an electrometer circuit and sensed by an oscilloscope, signal averager, or microprocessor. Coun-

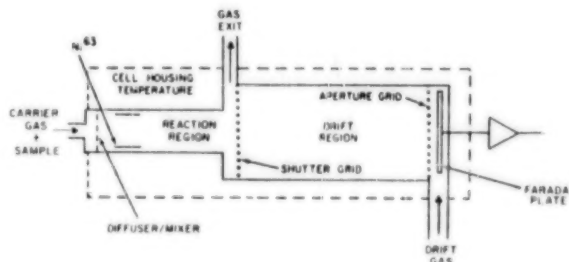


Figure 1. Ion Mobility Spectrometer.

terflowing in the drift region is a clean drift gas, entering near the collector and exiting near the shutter grid, which quenches reactions that continue in the drift region and distort the symmetry of the ion mobility peaks. The successful use of IMS requires exercising proper control on the composition and purity of the carrier and drift gases.

In simplest terms, IMS can be thought of as an Atmospheric Pressure Ionization (API) source coupled to an ion mobility drift tube. It is thus a cousin to Atmospheric Pressure Ionization Mass Spectrometry (API/MS).

IMS is further illustrated in Figure 2. The various ions (A, B and C) formed in the reactor are pulsed by the shutter grid into the drift region where they are separated (C, B and A) into ion mobility peaks (A, B and C). The separation occurs as the result of differences in the drift velocities for the various ions.

The theoretical relationships for the drift velocity are shown in Figure 3. The drift velocity is proportional to the electric field through a scalar parameter,  $K$ , known as mobility. Since the drift velocity is the drift length,  $d$ , divided by the drift time,  $t_d$ , of the ion to the collector, the mobility is the drift length divided by the drift time and electric field. That is, the mobility is inversely proportional to the drift time of the ion.

The mobility of gaseous ions in weak electric fields has been studied by Mason and Schamp (Mason and Schamp 1958, 1972). According to the core model of these authors, the mobility is inversely proportional to the collision cross section of the ion,  $\pi r_m^2 Q^{(1,1)*}$ , and the neutral gas density  $N$  as shown in Figure 4. To remove the effects of variable gas density, mobility can be normalized against temperature and pressure as shown in Figure 3. The result is reduced mobility. Reduced mo-

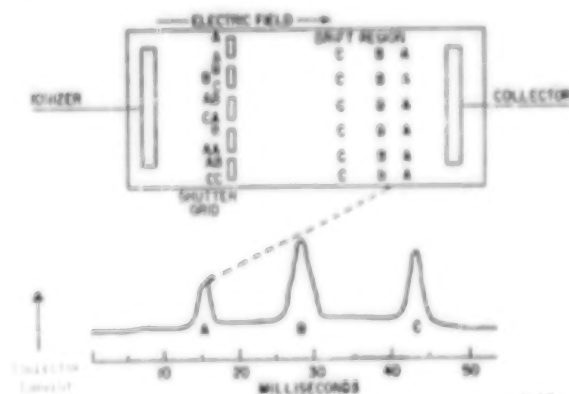


Figure 2. Ion Motion in Ion Mobility Spectrometry.

## DRIFT VELOCITY ( $V_d$ )

$$V_d = KE$$

## MOBILITY ( $K$ )

$$K = \frac{d}{t_d E}$$

## REDUCED MOBILITY ( $K_0$ )

$$K_0 = K \frac{P}{760} \cdot \frac{273}{T}$$

Figure 3. Relationship between Ion Velocity and Mobility.

bility is empirically related to the mass of the ion with larger ions having longer drift times and smaller ions having shorter drift times. However, because the correlation between drift time and mass is rough, IMS must be considered at best as a poor man's mass spectrometer. Ion mass information can only be obtained from IMS coupled to a mass spectrometer.

The Ion Mobility Spectrometer/Mass Spectrometer (IMS/MS) system at Bendix is shown in Figure 5. The system consists of a Bendix stacked ring IMS coupled to an Extranuclear SPECTREL mass spectrometer. The mass spectrometer is configured to accept an atmospheric pressure ioniza-

### MASON-SCHAMP THEORY FOR MOBILITY

$$\mu = \frac{3e}{16N} \left[ \frac{1}{m} + \frac{1}{M} \right]^{1/2} \times \left[ \frac{2\pi}{kT} \right]^{1/2} \times \frac{1}{\pi^{1/2} r_m^2 Q^{(1,1)*}}$$

WHERE

- $e$  = IONIC CHARGE
- $m$  = IONIC MASS
- $N$  = MOLECULAR NUMBER DENSITY
- $M$  = MOLECULAR MASS
- $k$  = BOLTZMANN CONSTANT
- $T$  = TEMPERATURE
- $r_m$  = POSITION OF MINIMUM POTENTIAL FOR INTERACTION
- $Q^{(1,1)*}$  = FIRST ORDER COLLISION INTEGRAL
- $\Delta$  = CORRECTION TERM FOR HIGHER APPROXIMATIONS

Figure 4. Mason-Schamp Theory for Mobility.

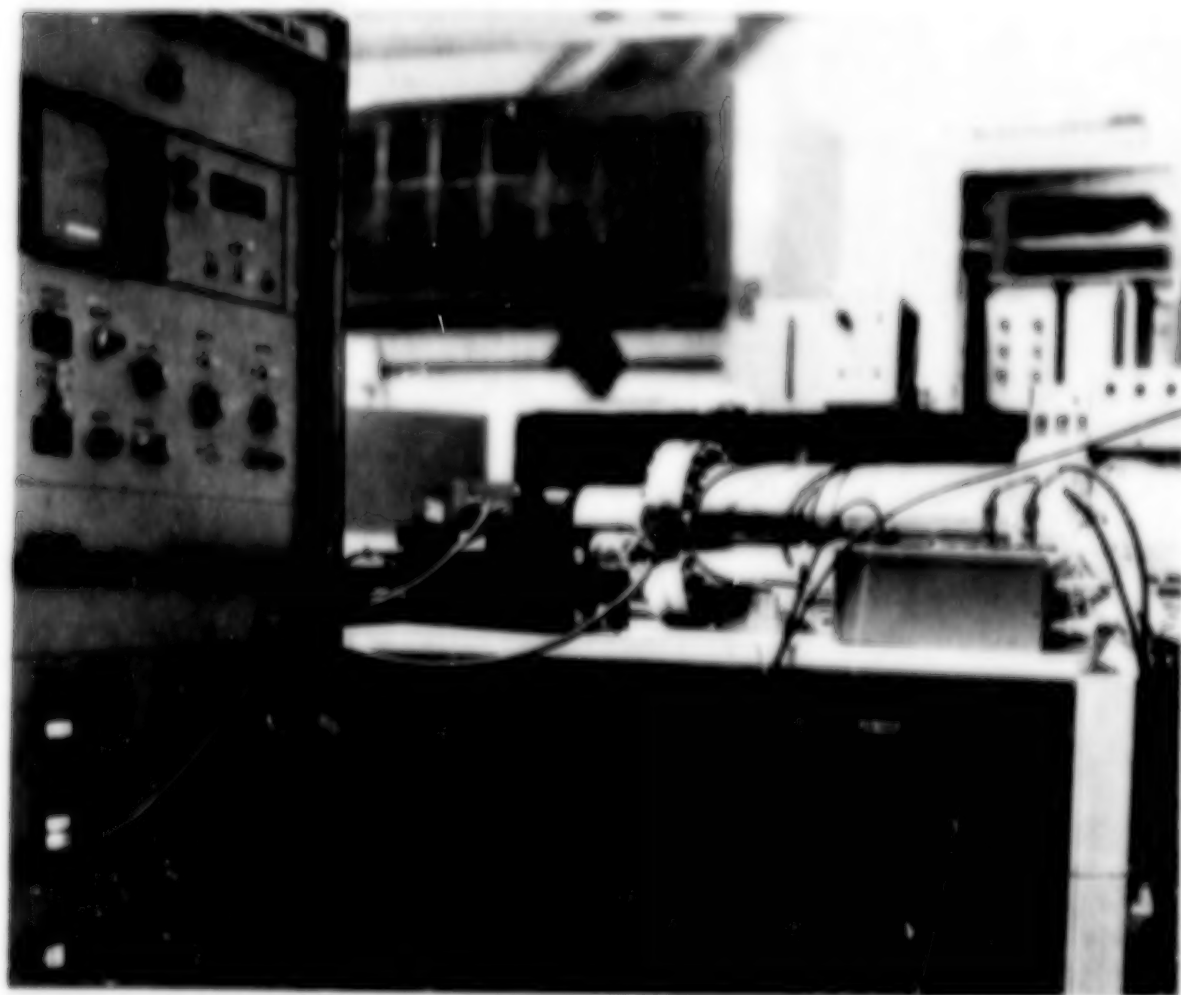


Figure 5. Ion Mobility Spectrometer/Mass Spectrometer System at Bendis.

tion source. The schematic layout of the system is shown in Figure 6. Provided in the collector of the IMS is a hole to allow passage of ions from the IMS to the MS. A potential is applied between the collector of the IMS and the 25 micron ion aperture into the high vacuum region of the MS. The ions pass from the IMS, through the collector, through the pinhole and into the API focusing lenses of the mass spectrometer. Two stage pumping is provided with a turbomolecular pump evacuating the inlet or ion optic section and diffusion pumps evacuating the analyzer or quadrupole filter section of the mass spectrometer.

Four types of data are available from IMS/MS as shown in Figure 7. The first is the ion mobility spectrum collected from the IMS. The second is the total ion mass spectrum collected with the shutter grid of the IMS open so that all ions generated in the IMS can be analyzed by the mass spectrometer. The third is the ion mobility spectrum

collected through the mass spectrometer operated in its total ion mode (dc voltage zero). The fourth is the mass identified mobility spectrum which is the ion mobility spectrum collected through the mass spectrometer tuned to a specific mass. Experimentally, ion mobility spectra are first collected from the IMS to obtain reduced mobility information. To correlate the ion mobility peaks with ion masses, this spectrum is then compared to the same spectrum collected through the mass spectrometer. By tuning the mass spectrometer to ions observed in the total ion (or API) mass spectrum, ion masses are correlated with ion mobility peaks via mass identified mobility data.

#### **Ion Mobility Spectra for Explosives**

Using IMS with a membrane inlet (Spangler, Suh, and Carrico 1980, Spangler and Carrico 1983), IMS signatures were collected on head space vapors from various explosives. The oper-

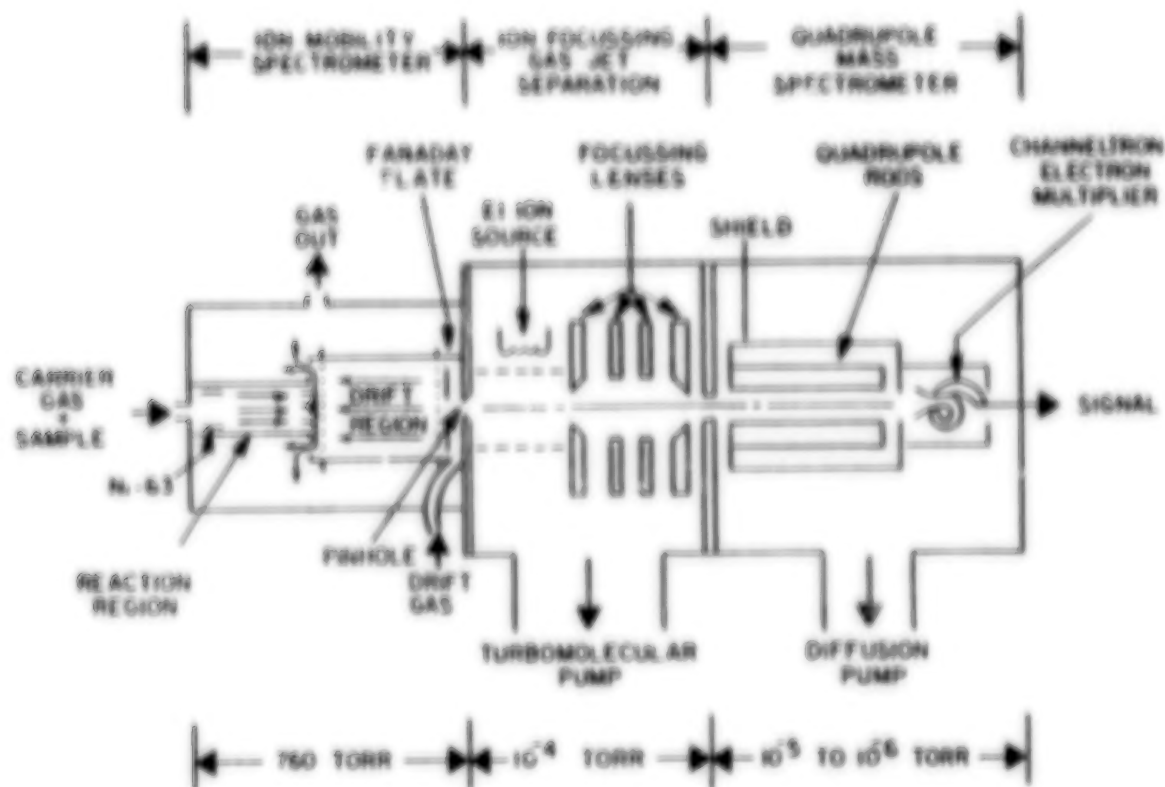


Figure 6. Schematic of Ion Mobility Spectrometer/Mass Spectrometer System.

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ating parameters for the IMS instrument are shown in Table 1. The drift housing temperature was 200°C, drift gas temperature was 106–112°C\*, inlet temperature was 227°C, the sample gas was ambient air, and the carrier and drift gases were purified air (approx. 4 ppm water or less) as generated by an AADCO Pure Air Generator.

Table 1. OPERATING PARAMETERS USED FOR THE ANALYSIS OF EXPLOSIVES WITH ION MOBILITY SPECTROMETRY

Ion Mobility Spectrometer	
CARRIER GAS	PURIFIED AIR
DRIFT GAS	PURIFIED AIR
SAMPLE GAS	AMBIENT AIR
MEMBRANE	DIMETHYLSILICONE
DRIFT FIELD	197 VOLT/CM
DRIFT HOUSING TEMPERATURE	200°C
DRIFT GAS TEMPERATURE	106–112°C*
INLET TEMPERATURE	227°C
SAMPLE GENERATION	SATURATED VAPOR
TEMPERATURE	PRESSURE AMBIENT

\* Drift gas temperature is less than the drift housing temperature because drift gas was not preheated.

The negative ion spectra for various explosives are shown in Figure 8. The top spectrum is the normal reactant ions ( $O^-$  or  $CO^-$  clustered with water). The other spectra are product ion spectra from which has been subtracted the reactant ions. The reactant ions are negative going peaks and the product ions are positive going peaks for these data. The results for composition B shown contributions from dinitrotoluene (DNT) and trinitrotoluene (TNT) but not cyclonite (RDX). RDX does not contribute to the composition B data because of the involatility of RDX in the vapor phase. The RDX results were obtained by flash evaporating RDX dust deposited on a solid sample probe inserted into the inlet. The spectrum for dynamite was obtained by sampling head space vapors. A

- ION MOBILITY SPECTRUM
- TOTAL ION MASS SPECTRUM
- TOTAL ION MOBILITY SPECTRUM
- MASS IDENTIFIED MOBILITY SPECTRUM

Figure 7. Types of Data Obtained from Ion Mobility Spectrometer/Mass Spectrometry.

more detailed discussion of these spectra will now follow.

Beginning with dynamite, the  $2.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  peak is not due to the explosive itself but rather to impurities of low electron affinity, (Spangler, Carrico and Campbell 1983). The peak of significance is the ion with reduced mobility  $2.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . This ion lies close to the reactant ion mobility peak (reduced mobility  $2.57 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and cannot be resolved from the reactant ion without reactant ion subtraction. A similar ion has been observed by other authors (Asselin 1978 and Wernlund, Cohen and Kindel 1978) with Wernlund, *et al.* identifying the ion as  $\text{NO}_2^-$  from IMS/MS data. The reactions leading to the formation of the  $\text{NO}_2^-$  are displayed in Figure 9. The  $\text{NO}_2^-$  ion may come from the nitroglycerin itself or from ethylene glycol dinitrate, an impurity in dynamite. As the temperature of the IMS is decreased, Figure 10 shows that the  $2.48 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  peak for dynamite disappears in favor of the  $1.37 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  peak (Wernlund, Cohen and Kindel 1978 and Spangler 1978). The  $1.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ion mobility peak for TNT is shown for reference in this figure. IMS/MS data show that the  $1.37 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  peak is nitroglycerin clustered with  $\text{NO}_2^-$  (Wernlund, Cohen and Kindel 1978). This result is consistent with the interpretation that ion attached moieties are more stable at reduced temperature because either the neutral molecule is more stable or the cluster is more stable. Wernlund, Cohen and Kindel showed that nitrate compounds dissociate easier as the number of nitrate groups increases (Wernlund, Cohen, and Kindel 1978).

For TNT, Figure 11 shows ion mobility spectra in air-nitrogen mixtures. With nitrogen carrier and drift gases, the major product ion is the  $\text{M}^-$  ( $m/z$  227) ion with reduced mobility of  $1.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . As laboratory air is allowed to enter the carrier gas, the  $1.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ion mobility peak decreases while the  $1.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ion mobility peak increases. The  $1.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ion has been shown with IMS/MS to be the proton abstracted ( $\text{M}-1$ ) ion. (Spangler and Lawless 1978). Figure 12 shows Negative Chemical Ionization Mass Spectrometer (NCIMS) data collected against TNT. For these data, the molecular negative ion is the major ion species. This ion arises because of the reduced pressure and the lack of oxygen or  $\text{NO}_2$  reactant ions in the mass spectrometer to perform the proton abstraction reaction. The ( $\text{M}-1$ ) ion was observed when the source pressure was increased to introduce these components. Figure 13

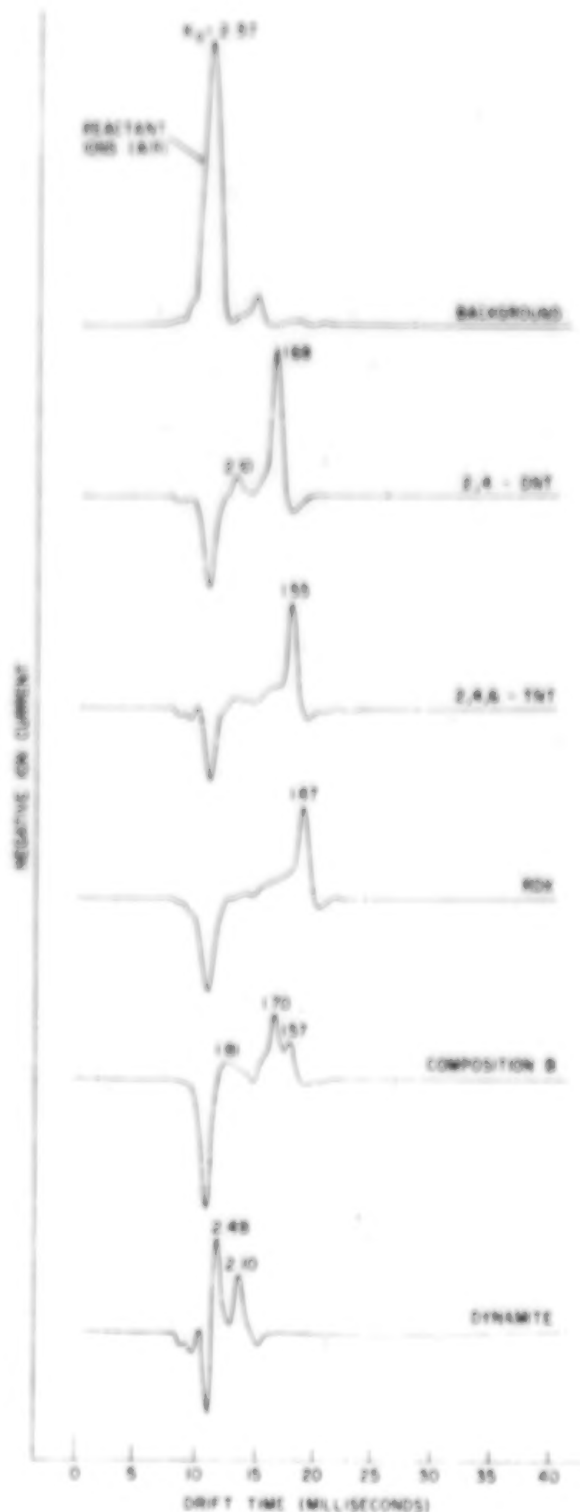


Figure 8. Negative Ion Mobility Signatures for Explosive Vapors Using Purified Air Chemistry. Upper Signature is Reactant Ion (Background). Other Signatures are Product Ion Signatures with Reactant Ion (Background) Subtraction.

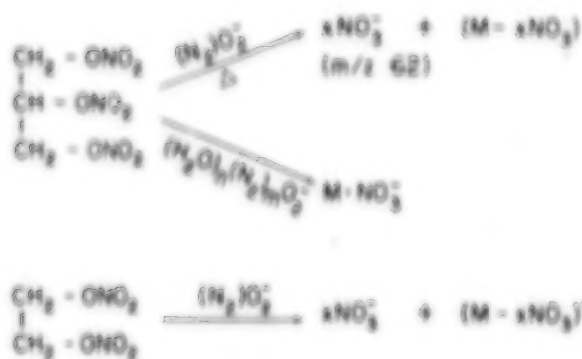


Figure 9. Ionization Scheme for Dynamite.

shows Negative Atmospheric Pressure Ionization Mass Spectrometer (NAPIMS) data collected on TNT. An  $\text{M}^+$  molecular ion is observed with nitrogen carrier gas and an  $(\text{M}-1)^+$  ion is observed with a purified air carrier gas. TNT undergoes two types of reactions as displayed in Figure 14. The product ion depends on whether nitrogen or air is used as carrier gas. Electron capture reactions occur in nitrogen and proton abstraction reactions occur in air.

For RDX, the operating parameters used for IMS/MS studies are displayed in Table 2. Since RDX is difficult to introduce into the instrument, the membrane inlet was modified, as shown in Figure 15, to include a wire probe insertion port. RDX sampling was accomplished by inserting a wire probe dusted with RDX into the heated ( $150^\circ\text{C}$ ) insertion port.

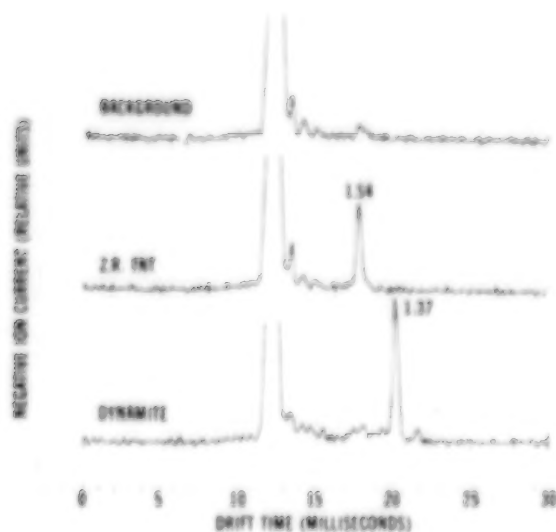


Figure 10. Ion Mobility Signatures for Trinitrotoluene (TNT) and Dynamite at Reduced Temperature ( $100^\circ\text{C}$ ). Carrier Gas—Laboratory Air, Drift Gas—Prepurified Nitrogen.

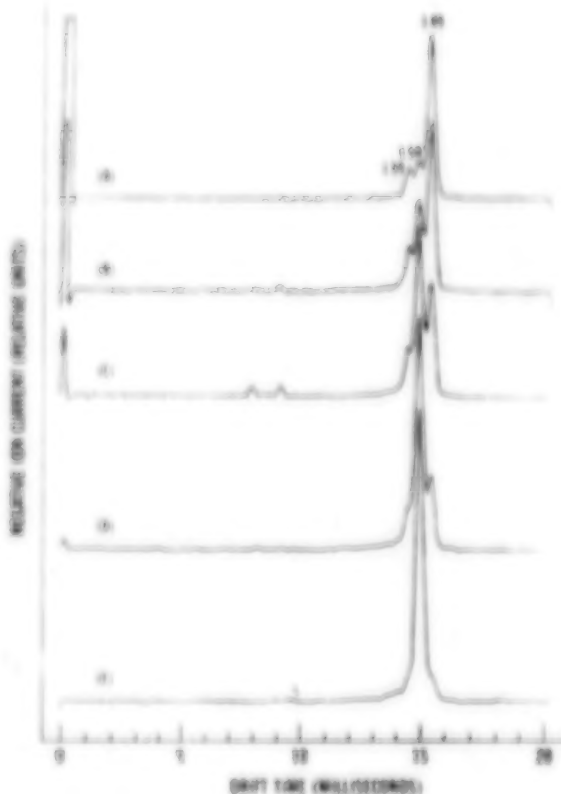


Figure 11. Ion Mobility Signature for 2,4,6-Trinitrotoluene in Air/Nitrogen Mixtures. Approximate (4% Accuracy) Mixture Percentages are: Spectrum A, 2% Laboratory Air; Spectrum B, 8% Laboratory Air; Spectrum C, 10% Laboratory Air; Spectrum D, 15% Laboratory Air; Spectrum E, 21% Laboratory Air.

Table 2. OPERATING PARAMETERS USED FOR THE ANALYSIS OF RDX WITH ION MOBILITY SPECTROMETER/MASS SPECTROMETRY

Ion Mobility Spectrometer	
CARRIER GAS	PURIFIED AIR
DRIFT GAS	PURIFIED AIR
SAMPLE GAS	AMBIENT AIR
MEMBRANE	DIMETHYLSILICONE
DRIFT FIELD	194 VOLT/MC
DRIFT TEMPERATURE	154°C
INLET TEMPERATURE	170°C
Mass Spectrometer	
PINHOLE APERTURE	25 $\mu\text{m}$
PRESSURE	
INLET (ION FOCUSING LENSES)	$1.6 \times 10^{-4}$ torr
CHAMBER (QUADRUPOLE MASS SPECTROMETER)	$4 \times 10^{-6}$
Sample	
GENERATION	DESORPTION IN HEATED INLET



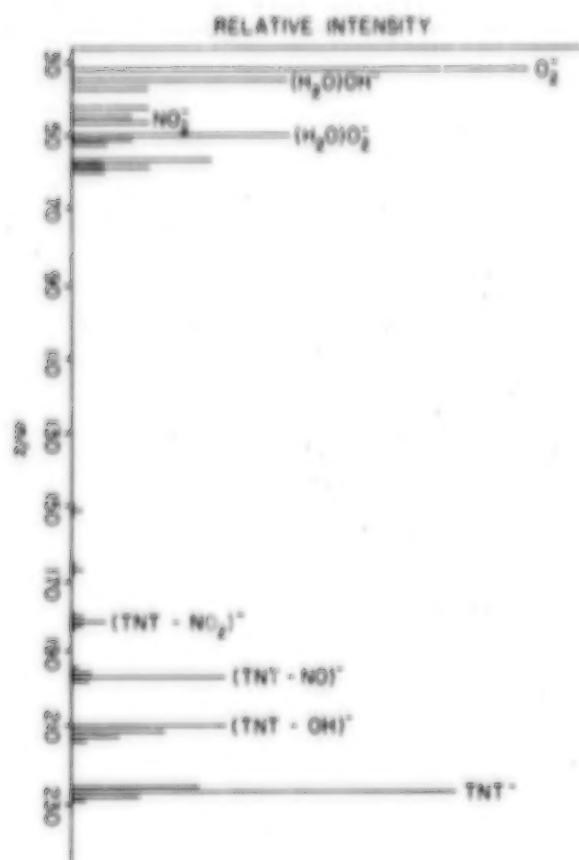


Figure 12. Negative Chemical Ionization Mass Spectrometry of 2,4,6-Trinitrotoluene.

Figure 16 shows the mass identified mobility data collected for the positive ions. The major ions are the  $m/z$  75 ion with its clusters contributing to the  $2.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ion mobility peak and the  $m/z$  176 ion with its clusters contributing to the  $1.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  ion mobility peak. Figure 17 shows the mass identified mobility data collected for the negative ions. An  $\text{NO}_2^-$  ion,  $m/z$  46, is spread out across the spectrum, a  $\text{M}^-$  ion clustered with water,  $m/z$  258, weakly contributes to an ion mobility peak with reduced mobility  $1.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and a  $(\text{M} + \text{NO}_2)^-$  ion clustered with water,  $m/z$  268, is a major ion species in the spectrum with a reduced mobility of  $1.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The ionization scheme for RDX is shown in Figures 18 and 19. In the positive ion mode, the proton attacks RDX at either the nitro-nitrogen or the amino-nitrogen giving rise to cleavages to produce the  $m/z$  75 or 176 ions respectively. In the negative ion mode, dissociative capture reactions lead to  $\text{NO}_2^-$  which undergoes ion attachment reactions to produce the  $(\text{M} + \text{NO}_2)^-$  ion.

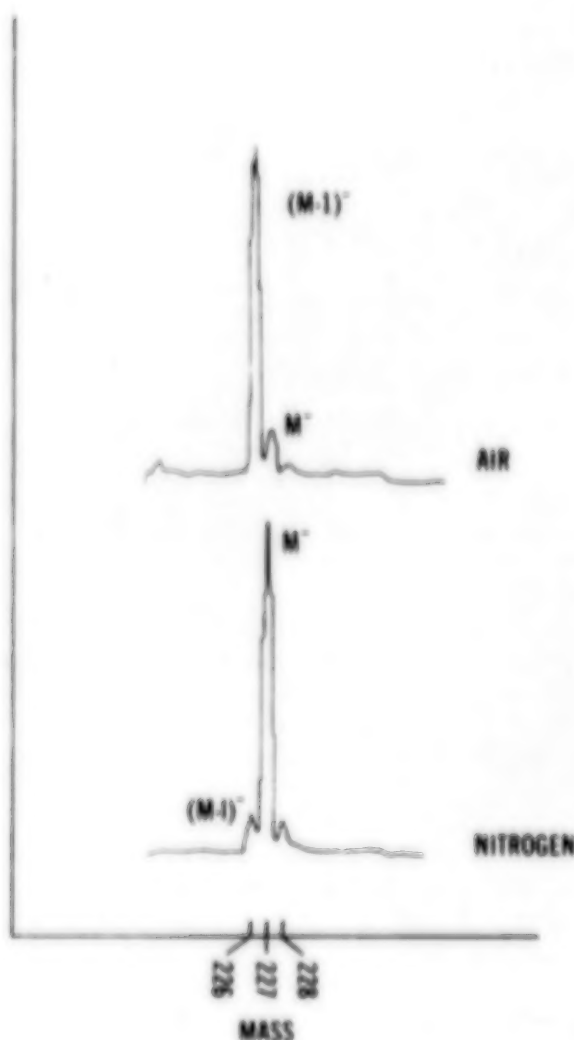


Figure 13. Negative Atmospheric Pressure Ionization Mass Spectrometry of 2,4,6-Trinitrotoluene. Upper Signature - Air Carrier Gas, Lower Signature - Nitrogen Carrier Gas.

#### Sample Introduction Techniques

Table 3 lists techniques whereby sample can be introduced into IMS. One approach is to use an ambient air carrier gas with a purified air drift gas. The ambient air is drawn into the reactor by ap-

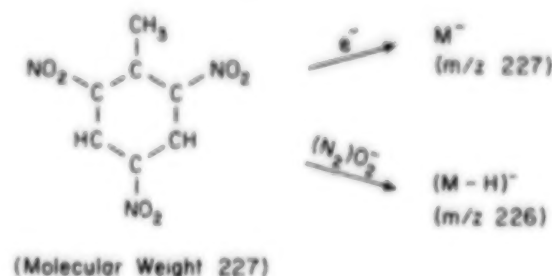


Figure 14. Ionization Scheme for 2,4,6-Trinitrotoluene.

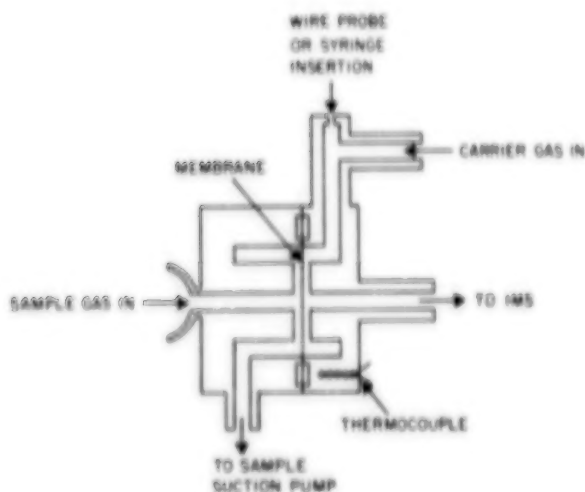


Figure 15. Modified Membrane Inlet with Probe Insertion Port.

plying suction to the gas exhaust port of the IMS cell. Sample is introduced into the ambient air carrier gas for analysis purposes. The early analysis of TNT vapor was accomplished by using this technique (Spangler and Lawless 1973).

A second generation beyond the ambient air carrier is the membrane inlet where ambient air is used as sample gas and purified air is used as carrier gas (Figure 20). The ambient air scrubs the external surface of the membrane and the carrier gas scrubs the internal surface of the membrane. Sample permeates through the membrane from the sample gas to the carrier gas. The membrane inlet was used for the analyses performed in connection with Figure 8.

Table 3. SAMPLE INTRODUCTION TECHNIQUES

- AMBIENT AIR CARRIER GAS
- MEMBRANE INLET
  - AMBIENT AIR SAMPLE GAS
  - PURIFIED AIR CARRIER GAS
- SAMPLE WIRE PROBE/SYRINGE
  - SOLVENT EXTRACTION
  - SOLVENT EVAPORATION
  - ADSORPTION/DESORPTION
- SOLIDS PROBE
- DESORPTION OVEN
- SURFACE SAMPLER
  - THERMAL
  - JET SCRUBBING
- EXPONENTIAL DILUTION FLASK
- STANDARDS GENERATOR
  - BUBBLER
  - DIFFUSION TUBE
  - PERMEATION TUBE
- GAS CHROMATOGRAPHY

Compatible with both the ambient air carrier gas and membrane inlet is the sample wire probe

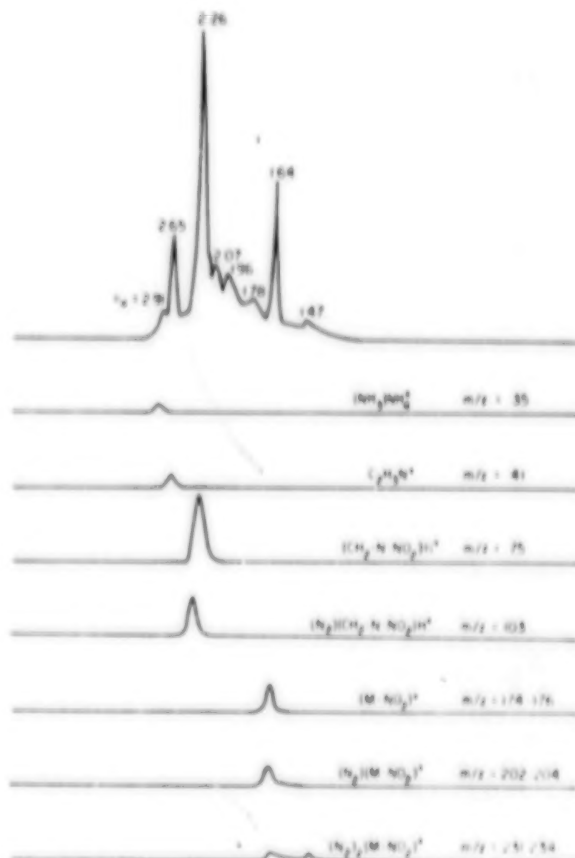


Figure 16. Mass Identified Mobility Data for the Positive Ions of RDX.

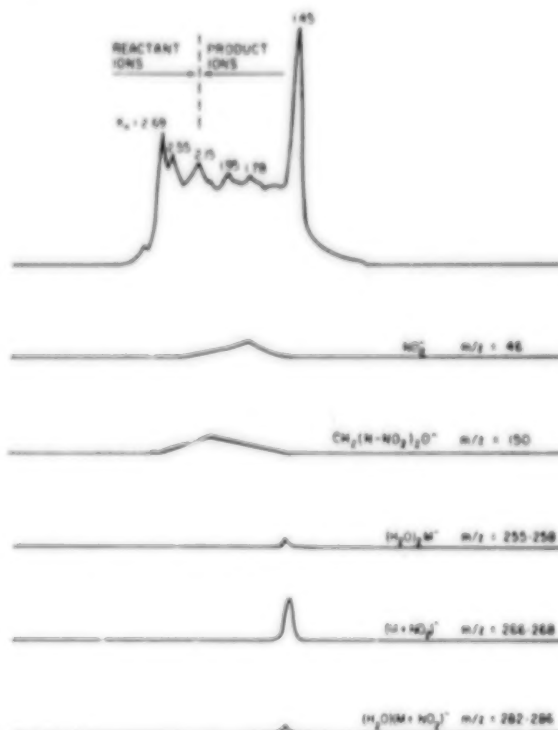


Figure 17. Mass Identified Mobility Data for the Negative Ions of RDX.

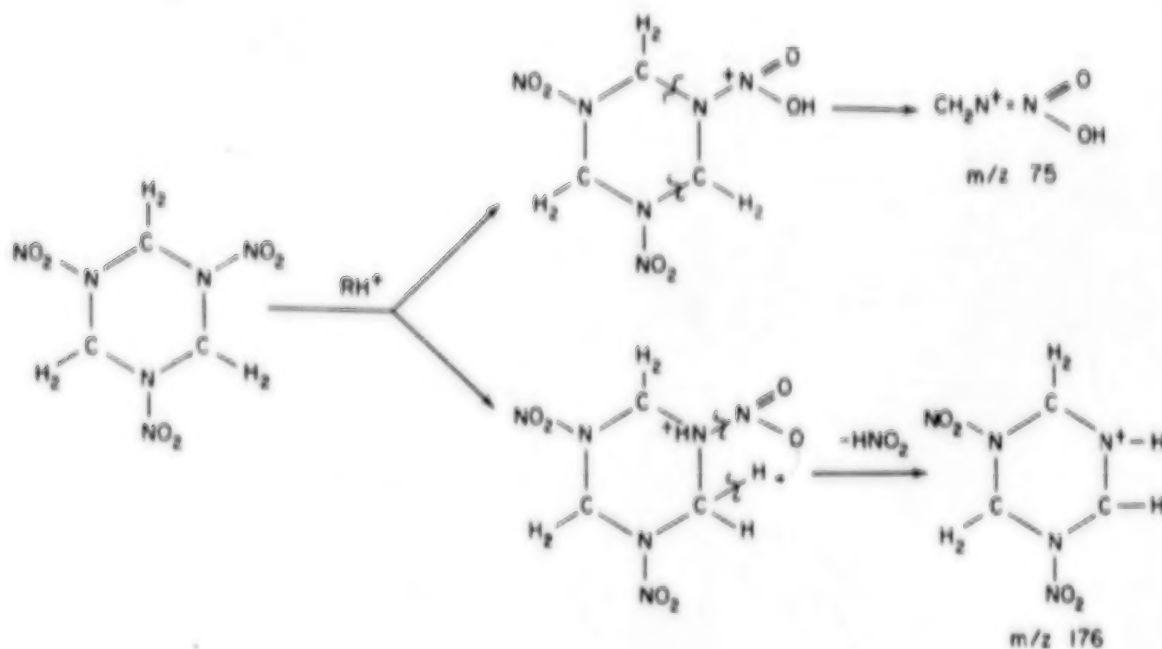


Figure 18. Positive Ionization Scheme for RDX.

and/or syringe. When used by itself, the sample wire probe collects vapor by adsorption and the vapor is desorbed when the wire probe is inserted into the heated inlet. When used with syringe, solvent extracts of the sample can be deposited on the wire probe which, after solvent evaporation, can be inserted into the heated inlet for sample desorption. The sample wire probe was used to collect the data of Figures 16 and 17.

The sample wire probe and/or syringe can also be used to introduce sample into a purified air carrier gas without the use of a membrane. As illustrated in Figure 21, this is accomplished by covering the inlet with a glass tube through which a hole is provided for insertion of the wire probe. Carrier

gas flowing along the internal surface of the glass tube and into the IMS transports vapor desorbed from the wire probe into the IMS. The technique corresponds to on-stream injection in gas chromatography.

A variation of the sample wire probe is the solids probe. Figure 22 shows a solids probe for sampling soil. It consists of an 0.25 inch diameter stainless steel tube specially configured to accept the soil particles. Sample air for the IMS flows through the stainless steel tube, across the soil particles, and into the IMS. The experiment consists of exposing the soil particles to head space vapors of TNT, placing the soil particles in the solids probe, and inserting the solids probe into the heated inlet of the instrument. Desorption of vapor from the soil particles yields a strong response from the IMS instrument.

The desorption oven technique consists of flowing carrier gas through a sealed oven before entering the IMS. Materials to be sampled are placed in the oven and heated. Vapors released from the sample materials are then carried into the IMS by the carrier gas. Carr and Needham used this technique to study impurities on silicon discs (Carr and Needham 1979). The technique is also used at Bendix to screen materials for IMS construction.

The exponential dilution flask and standards generator techniques are calibration techniques. The exponential dilution flask was used to establish the basic limit of detection of 0.1 ppt for IMS

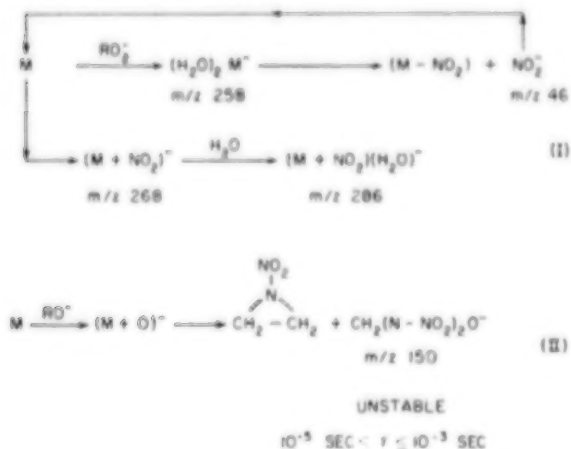


Figure 19. Negative Ionization Scheme for RDX.

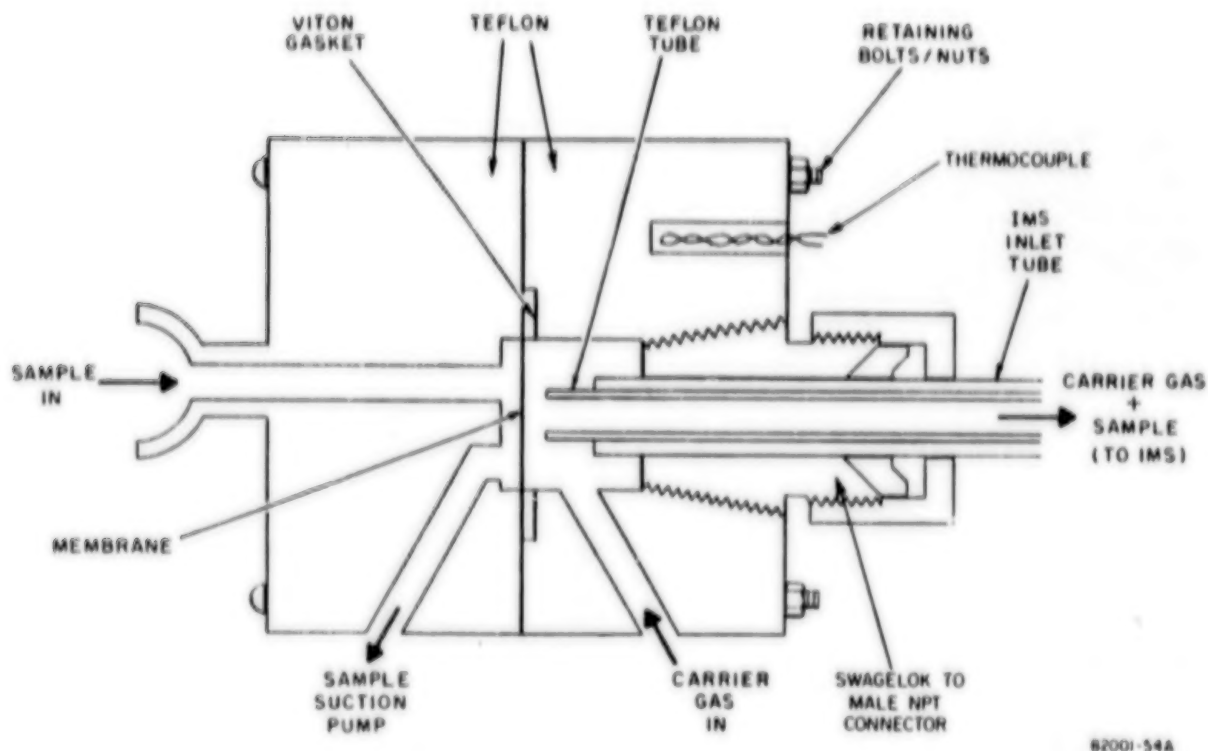


Figure 20. Membrane Inlet System for Ion Mobility Spectrometry.

to TNT vapor (Spangler and Lawless 1978). Diffusion tube generators have been used to establish the limit of detection of approximately 1 ppb for IMS (with a membrane inlet) to organophosphorous vapors (Carrico, Campbell, and Spangler 1983).

#### Ion Mobility Detector System

A compact IMS system with a membrane inlet is displayed in Figure 23. The system is 0.6 cu. ft. in volume, weighs less than 30 pounds and is microprocessor controlled. The system requires a 28 volt power supply for operation and draws under 50 watts. It can be carried very easily by one man with the handle/roll-bar.

The pneumatic and electronic layout for the system is illustrated in Figure 24. A closed loop is provided for the carrier and drift gases. A pump

circulates the gases through a molecular sieve trap to purify them before entering the IMS. The membrane isolates the ambient air from the internal workings of the IMS cell. Thus the water, ammonia,  $\text{NO}_x$  and halogenated vapor components of ambient air are excluded from the reactor of IMS. These problem vapors influence the ion/molecule reactions needed to ionize sample. IMS/MS data on the nature of reactant ions in IMS using a membrane inlet is submitted for publication (Spangler and Carrico 1983).

The top panel of the compact IMS of Figure 23 is shown in Figure 25. The sample port going to the membrane enters through this panel. The LED readout is operator accessed to determine the state of the instrument and to specify the compound giving rise to an alarm. Compounds are specified by the microprocessor from features of the ion mobility spectrum. An alarm horn provides an audible alarm in the presence of targeted vapor. Outputs are available for oscilloscope or signal averager display. An RS232 interface is available to transmit IMS signatures over telephone lines from the system to a host computer.

Surface sampling can be accomplished by attaching a surface sampler to the inlet of the system of Figure 23 as illustrated in Figure 26. The function of the surface sampler is to heat the sample on

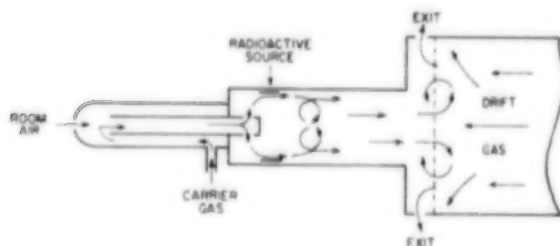


Figure 21. Wire Probe Insertion Inlet with Postulated Flows.

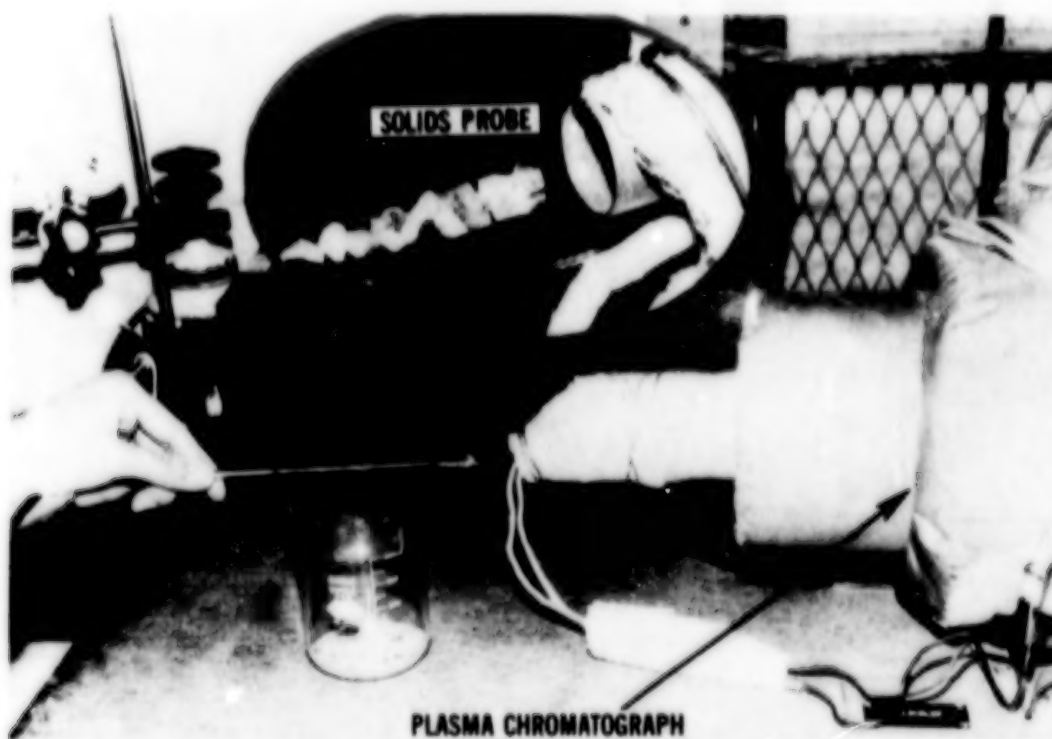


Figure 22. Solids Probe for the Analysis of Explosive Vapors Adsorbed on Soil Particles.



Figure 23. A Compact Ion Mobility Detector System for Monitoring Ambient Air.

# SYSTEMS DIAGRAM

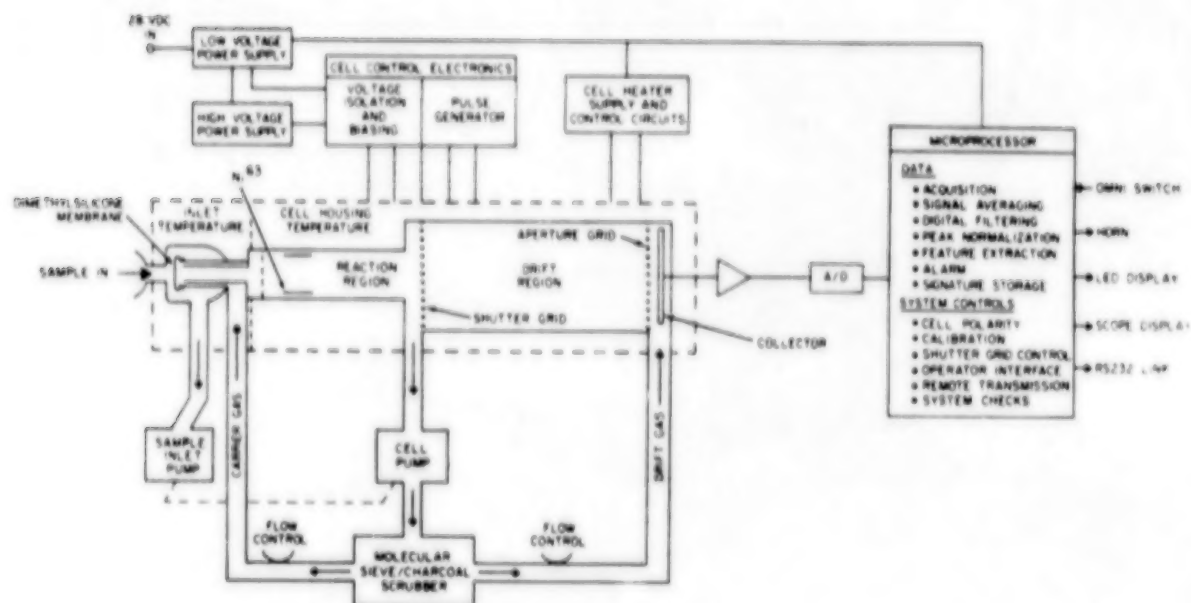


Figure 24. The Pneumatic and Electronic Layout for the System of Figure 23.

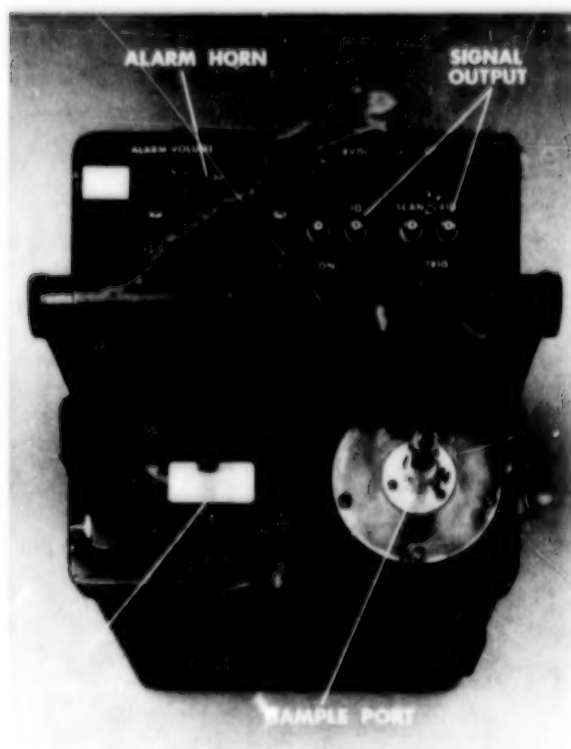


Figure 25. Top Panel for the System of Figure 23.

the surface and transport the released vapors to the detector which functions as a normal alarm. A closer view of the surface sampler is presented in Figure 27 and an internal schematic is shown in

Figure 28. In the sampler is a tungsten halogen lamp to heat the surface and air jets to cause turbulence in the sampler cone. The sample released from the surface swirls up into the transport lines



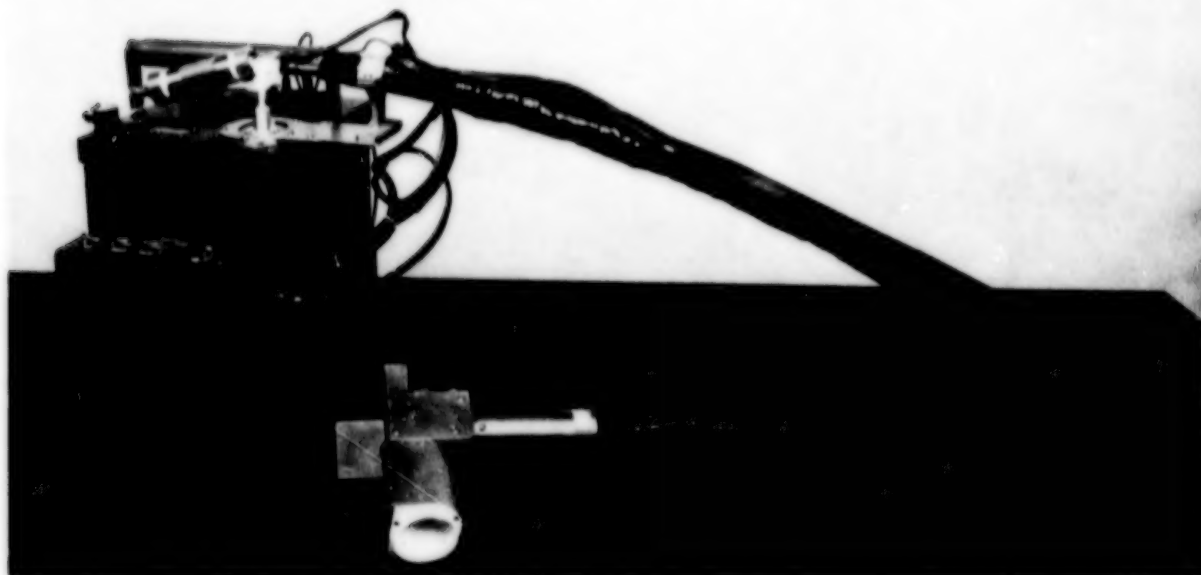


Figure 26. Surface Sampler Attached to the Inlet of the System of Figure 23.

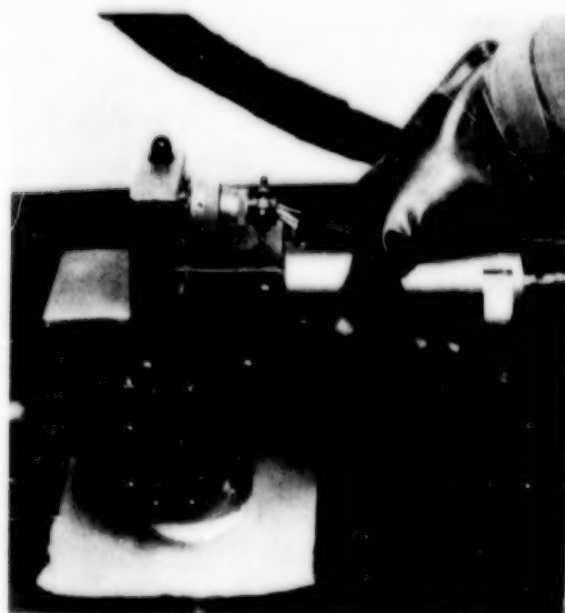


Figure 27. Close-Up View of the Surface Sampler.

which carry the sample to the detector.

Figure 29 illustrates the theoretical considerations underlying the design of the surface sampler. A high flow of gas is maintained across the surface to reduce stagnant boundary layers which impede the flow of released vapors. As given by the diffusion equation, the flux,  $J_v$ , of vapor across the boundary layer,  $\delta$ , is proportional to the square root of gas velocity. Because the concentration of vapor delivered to the detector is the flux divided by the gas velocity, the sample concentration

sensed by the detector is inversely proportional to the square root of the gas velocity. To both maintain high velocities required to reduce boundary layer effects while at the same time to maintain low velocities required to minimize sample dilution effects, localized air jets are used to scrub the surface.

The concentration term  $(n_s - n_\infty)$  of  $J_v$  is the gradient which drives the vapor release. This term is temperature sensitive since  $n_s$  corresponds to the equilibrium vapor pressure of sample at surface

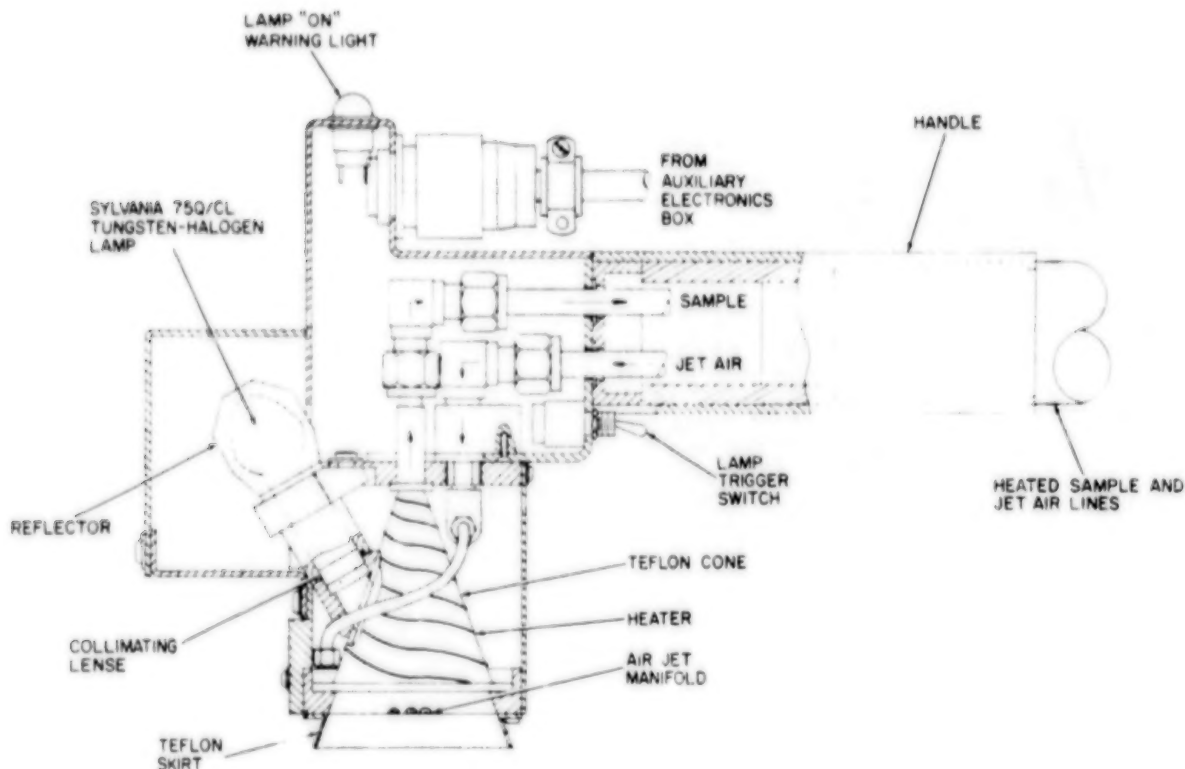
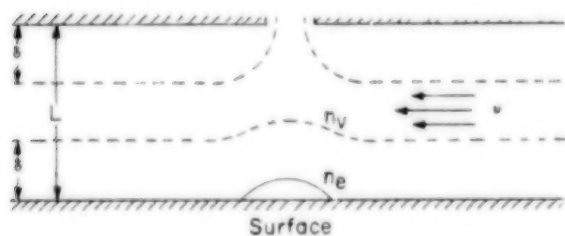


Figure 28. Internal Drawing of the Surface Sampler.

temperature. The tungsten-halogen lamp increases the surface, and hence sample temperature, to increase  $n_e$ . Such an increase leads to greater sampling efficiency for the surface sampler.

Finally, the flux  $J_s$  is inversely proportional to the dimension  $L$  of the channel in which the gas flows. A collapsed geometry for the sampler cone,



LANGMUIR DIFFUSION EQUATION

$$J_v = -\frac{D}{b} [n_e - n_v]$$

VISCOUS BOUNDARY LAYER

$$b = \frac{5L}{\sqrt{R}} \quad \text{where } R = \frac{\rho v L}{\mu}$$

THEREFORE

$$J_v = -\frac{D}{5} \sqrt{\frac{\rho v}{\mu L}} [n_e - n_v]$$

Figure 29. Theoretical Considerations for the Operation of the Surface Sampler.

where  $L$  is small, is preferred over open geometry. This is illustrated in Figure 30 where configuration A is preferred over configuration B. In practice, however, the greater effectiveness obtained from jet scrubbing (configuration C) and heating with

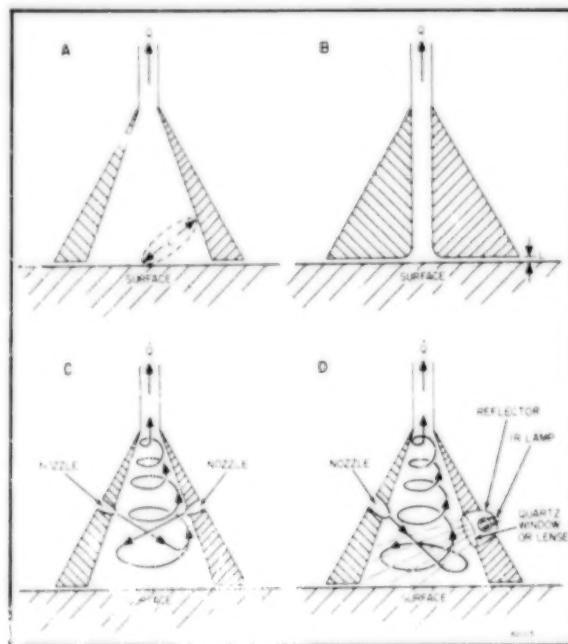


Figure 30. Surface Sampler Cone Geometry.

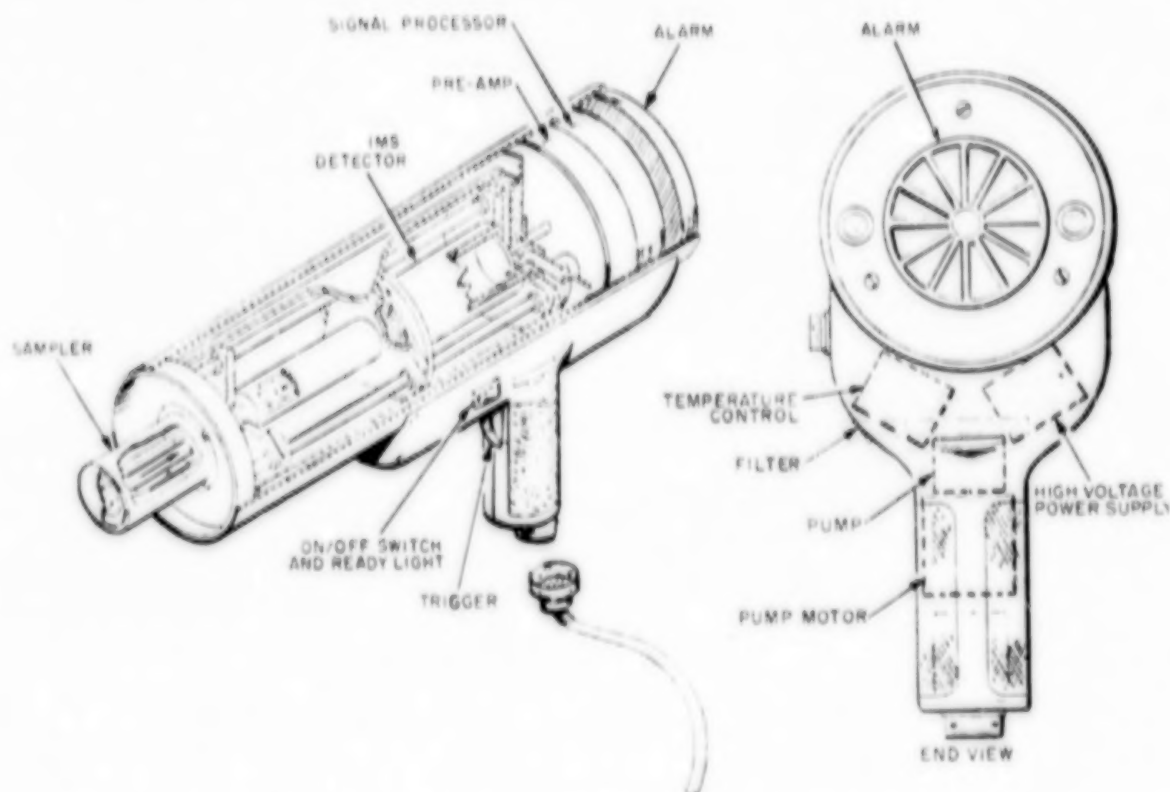


Figure 31. Surface Sampler Closely Coupled to a Hand-Held Ion Mobility Spectrometer.

the tungsten-halogen lamp (configuration D) exceeds the losses associated with the open geometry needed to implement these techniques. Between jet scrubbing and heating, heating was found more effective depending on surface composition.

Finally, Figure 31 shows a surface sampler closely coupled to an IMS in an hand held configuration. The direct coupling between the surface sampler and IMS cuts down transmission losses for the vapors through connecting tubes.

#### Acknowledgements

The authors wish to acknowledge G. Sima, K. Vora, J. White and J. Roehl as the principal engineers for the design of the compact IMS system. The authors wish to acknowledge G. Lozos for the design and testing of the surface sampler. The encouragement and interest of D. Campbell during the development efforts is acknowledged.

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**HIGH PERFORMANCE LIQUID  
CHROMATOGRAPHY METHODS**





# THE ANALYSIS OF ETHYLENEGlyCOLMONONITRATE AND MONOMETHYLAMINE NITRATE FROM COMMERCIAL BLASTING AGENTS IN POST BLAST SAMPLES

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**ABSTRACT.** The analysis for ethyleneglycolmononitrate and monomethylamine nitrate in commercial blasting agents and post blast samples has been done. The commercial blasting agents, POWERMEX (C.I.L.) and TOVEX (DuPont) have been encountered in an number of seized, disrupted or hoax explosive devices and have been suspected in a number of bombing incidents. Work has been done to develop a procedure to detect the sensitizers ethyleneglycolmononitrate (EGMN) from Powermex and monomethylamine nitrate (MMAN) from Tovex using high performance liquid chromatography. Analysis of samples of debris recovered from test blasts has been successful after using an appropriate pre-concentration technique.

## INTRODUCTION

Powermex® and Tovex® are commercial blasting agents available in Canada for about 10 years. Although marketed as replacements for dynamite they have not succeeded in displacing its popularity particularly in the criminal community. Nevertheless, they have been found amongst explosives confiscated from motorcycle gangs and have been suspected in a number of bombings in labour related incidents in areas where there is ready access to these particular products. Thus a method of analysis is needed.

Powermex® and Tovex® are sensitized with ethyleneglycolmononitrate (EGMN) and monomethylamine nitrate (MMAN) respectively. The purpose of this project was to develop a technique for the qualitative identification of small amounts of EGMN and MMAN and to determine whether detectable amounts of these sensitizers can be found in post blast debris. Further, it is desirable that the method be compatible with that devised for the analysis of dynamite residues previously reported by Prime and Krebs (1980).

Because it is chemically similar to ethyleneglycoldinitrate (EGDN) and nitroglycerine, EGMN can be identified following a procedure analogous to that described for dynamite. On the other hand, MMAN is a chemically unrelated compound.

The identification of MMAN in large samples can be done by X-ray diffraction and infra-red

spectrophotometry. However, for smaller amounts dispersed in explosion debris, the recovery and identification of MMAN is more difficult. Parker (1975) has described some properties of MMAN and spot tests for identification; also the literature [Kawata *et al.* (1980) and Blau and King (1978)] suggests a variety of methods for the analysis of amines by both gas chromatography and derivative high performance liquid chromatography (HPLC). A procedure involving extraction and derivatization of the monomethylamine for subsequent identification by HPLC was selected.

## EXPERIMENTAL

### Equipment and Materials

A Waters ALC 202 liquid chromatographic system with 6000A pumps, a model 660 solvent programmer, and a U6K septumless injector (Waters Associates, Milford, Mass.) was used. A variable wavelength Spectromonitor II model 1202 (LDC, Riviera Beach, Florida) UV-visible detector was used.

Solvents were HPLC-grade supplied by Caledon (Georgetown, Ont.), filtered and degassed by suction through 0.5  $\mu$  Teflon filters (Millipore, Bedford, Mass.). Water used for chromatography was glass distilled and organic contamination was removed with a Norganic cartridge (Millipore).

Columns were  $\mu$ -Bondapak-CN and  $\mu$ -Bonda-

pak-C<sub>18</sub> (Waters Assoc.) supplied prepacked in 3.9 mm x 30 cm stainless steel.

EGMN, MMAN were prepared as standards in this laboratory. The explosives were 1' x 12" sticks of CIL Powermex<sup>®</sup> 300 and Dupont Tovex<sup>®</sup> 5000 SB initiated with No. 8 electric blasting caps.

Dansyl chloride (Fisher Scientific, Toronto) was used as supplied.

#### Tests

Two separate blast sites were used to provide different types of debris.

(a) Single sticks of blasting agent were detonated on clean sand. Samples were collected from the base and edges of the crater to a depth of 2-3 cm and stored in 1 l Mason jars.

(b) To simulate a common explosion site, a four foot square wooden frame was constructed of 2" x 4" lumber with studs at 16" centre. The spaces were filled with R-12 fiberglass insulation and the unit covered with drywall. The single sticks of blasting agent were taped to the centre of the drywall, draped with curtain and detonated. Samples of fiberglass and drapery were collected from the edges of the seat.

#### Procedure

##### i. Ethyleneglycolmononitrate

Samples to be tested were purged for 1 hr. with N<sub>2</sub> at room temperature and at 65 °C and the effluent collected on charcoal using a 700 ml glass apparatus as previously described for the recovery of EGDN and nitroglycerine by Prime and Krebs (1980). Each trap was washed with 1 ml of 2-propanol which was then filtered through a 0.5 µ Teflon filter. A 5 µl portion of this was run directly on HPLC. The remainder was concentrated, when necessary, by evaporation under an air stream being careful not to take to dryness.

##### ii. Monomethylamine nitrate

A 500 to 700 cc portion of the material from the seat of the explosion was washed with a minimum of distilled water (usually 50 to 100 ml) and filtered. The solution was made acidic with hydrochloric acid, then taken to dryness on a steam bath. The residue was re-dissolved in 1 ml water and added to 3 ml of DnsCl in acetone. Na<sub>2</sub>CO<sub>3</sub> was added to make the solution basic (usually 10 mg) and the mixture shaken vigorously; then, stored at 45 °C for 30 min. in darkness. The Dns derivative was recovered by extraction with 5 ml

µ BONDAPAK C<sub>18</sub>  
200 nm  
50:50 acetonitrile:water

µ BONDAPAK CN  
254 nm  
70:30 hexane:chloroform

µ BONDAPAK CN  
214 nm  
90:10 hexane:isopropanol

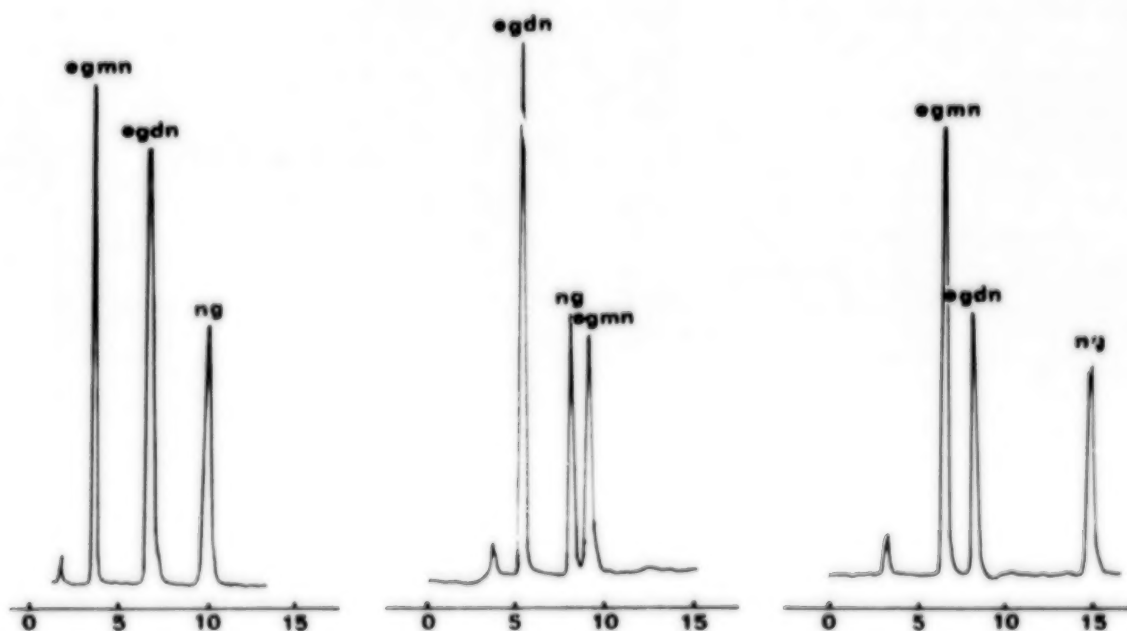
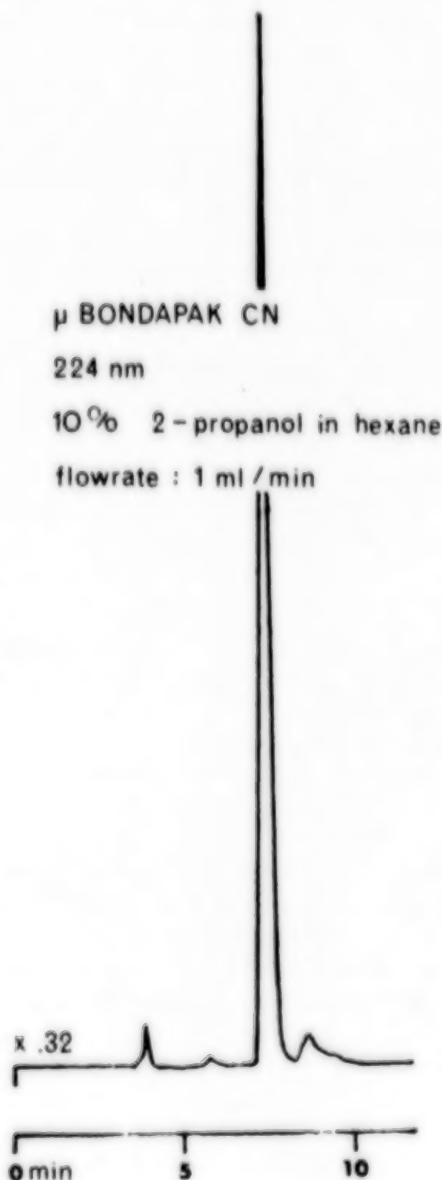


Figure 1. Separation of EGMN, EGDN and nitroglycerine using various chromatographic conditions.

of n-heptane which was evaporated on a steam bath. The residue was taken into 1 ml acetonitrile. A 5  $\mu$ l portion of this was injected into the liquid chromatograph.

## RESULTS AND DISCUSSION

Figure 1 shows the separation of EGMN, EGDN and nitroglycerine using various chroma-



Éthyleneglycolmononitrate recovered from fiberglass debris after a POWERMEX test blast

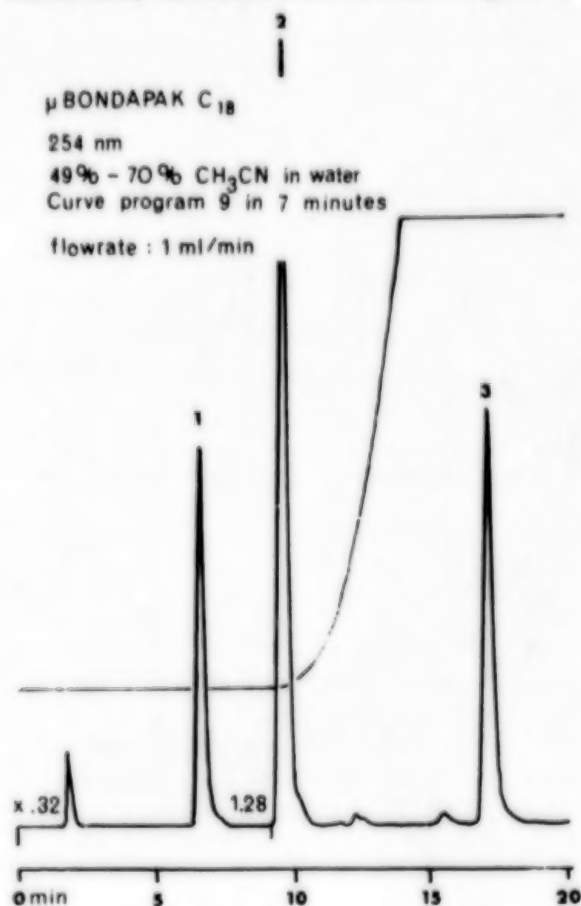
Figure 2. EGMN recovered from fiberglass debris after a Powermex® test blast.

tographic conditions. The sensitivity for these compounds is increased at lower wavelengths, therefore, the choice of wavelength is governed by the transparency of the mobile phase.

EGMN was recovered from samples in both tests and Figure 2 shows the recovery of EGMN from fiberglass. Recovery of EGMN was enhanced by at least a factor of 4 by purging at 65°C. In the general approach to recovery, a room temperature purge of explosion debris is still a worthwhile step, particularly, for samples that are likely to contribute interfering contamination on heating.

Verification of EGMN can be made by altering the chromatographic conditions as seen in Figure 1 or by gas chromatography, Yip (1982).

Figure 3 shows the separation of the methylamine dansyl derivative from the excess reagent. A



Dansyl derivatives of extract of fiberglass debris from TOVEX blast: 1. ammonia 2. methylamine 3. reagent

Figure 3. Dansyl derivatives of extracts of fiberglass debris from a Tovex® test blast: 1. ammonia 2. methylamine 3. reagent.

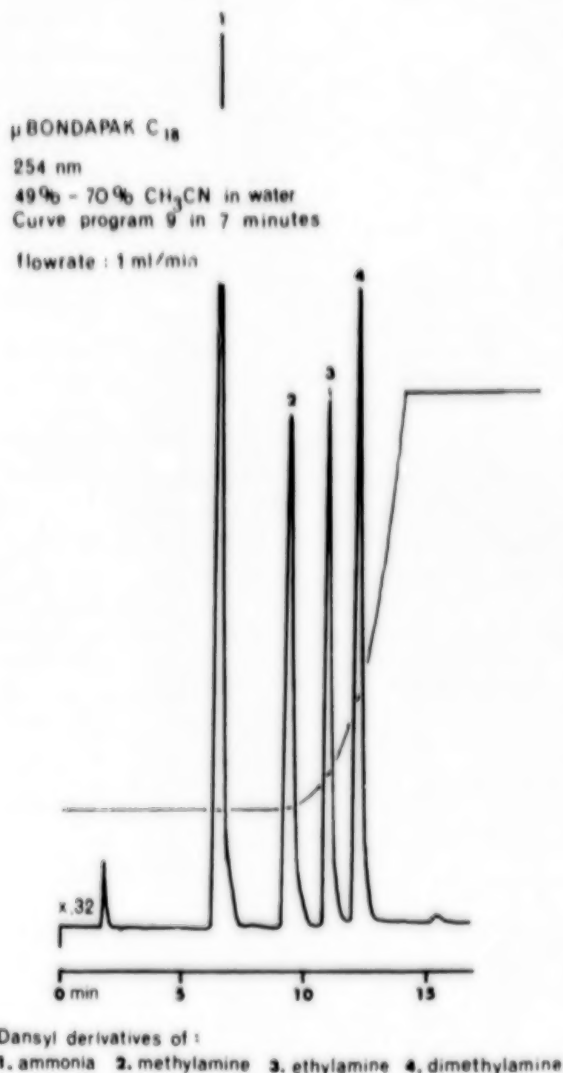


Figure 4. Dansyl derivatives of: 1. ammonia 2. methylamine 3. ethylamine 4. dimethylamine.

peak often appears for the ammonia derivative due to the ammonium nitrate in Tovex® but presents no problems.

Unlike EGMN, EGDN and nitroglycerine, primary amines are not specific to explosive substances. Thus it is particularly important that comparison samples unaffected by the blast be examined before conclusions are reached. Other low molecular weight aliphatic amines were de-

rivativized and could be separated from the methylamine derivative by HPLC as seen in Figure 4.

The general approach to explosive debris allows for the recovery of EGMN, EGDN and nitroglycerine by the purge and trap procedure followed by extraction with water for MMAN. Since nitrate crystals, and other physical evidence are often useful to the investigation, a microscopic examination is necessary. This can be accommodated after the purge and before the extraction step since MMAN is not volatile.

Of further interest from the test blasts was the fact that without a booster charge Tovex® very often did not detonate completely and pieces were sometimes visible in the debris or as smears on the drywall surface. Furthermore, both Tovex® and Powermex® left numerous fragments of plastic wrapper many of which had useful identification value.

## CONCLUSION

EGMN and MMAN can be recovered from explosion debris by a procedure that is compatible with that used for the recovery of the explosive oils of dynamite which are more commonly encountered.

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## ANALYSIS OF EXPLOSIVES BY HPLC-FTIR

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**ABSTRACT.** High pressure liquid chromatography (HPLC) is gradually supplanting thin layer chromatography (TLC) as a tool in the identification of explosive residues. Debris from explosion scenes is often extracted using bulk solvents or by headspace concentration and analyzed by HPLC. Identifications are based on comparison of retention time data with known standards. It would be desirable, however, to develop a more specific method for identification of these eluants using Fourier Transform Infrared Spectroscopy (FTIR). The tremendous separatory power of HPLC allows the analyst to "prep" each component of the explosive residue in suitable purity and quantities to generate useful infrared spectra. Normal phase HPLC with 3 micron silica columns is particularly useful because eluants are then composed of organic solvents which are readily evaporated to yield a film on KBr plates or a pressed KBr pellet of the sample. Since FTIR has proven to be considerably more sensitive than dispersive IR, the FTIR systems can be used as a real-time chromatographic detector. Using ultra-micro HPLC flowcells (0.2  $\mu$ l volume) as detector cells, the FTIR becomes an on-the-fly detector. Special software, such as the Nicolet chemigram programs, and liquid nitrogen cooled Mercury Cadmium Telluride detectors serve to provide a very selective detector sensitive only to changes in absorptions in a narrow infrared wavelength region. Alternatively, the full spectra can be taken of the eluant on-the-fly. Subtraction routines then can be used on this data to remove the contribution the eluant solvents to the eluate spectrum. The resultant spectrum then can be confirmed by comparison with reference spectra via a computer library search of various standard explosive infrared spectra.

### INTRODUCTION

The criminal use of explosives appears to be on the rise in this state. Recently there have been two bomb-related deaths, one exploding device in an automobile causing permanent injury, and a number of "damage to property" cases. This trend has prompted a search for improvements in the analysis of explosive residues.

One such improvement is the use of high pressure liquid chromatography (HPLC) to aid in the screening and identification of commonly encountered explosives. Both normal and reversed phase separations with UV detection for the nitroaromatics, nitrate esters and nitramines have previously been reported.<sup>1-4</sup> In this laboratory HPLC has been augmenting analysis schemes using TLC, IR, XRD, chemical spot tests and microchemical

tests similar to those already demonstrated.<sup>5-10</sup> Debris from explosion scenes are usually extracted using bulk solvents or by headspace concentration<sup>11</sup> and analyzed by HPLC using retention time data for identification.

UV detection at 254 nm is a relatively non-selective technique because many other compounds, such as asphaltics, plasticizers and other co-extractables, absorb at that wavelength to give a detector response. A recent improvement in HPLC selectivity has been proposed by interfacing the chromatograph with a Fourier transform infrared spectrometer (FTIR).<sup>12,13</sup> Wavelengths characteristic of functional group absorptions in certain explosives would give confirmation of the unknowns' identity when combined with the retention time as the component elutes from the ana-



lytical column. Furthermore, it would be even more desirable to generate a complete IR spectrum of the component. By subtracting absorptions due to solvent, it is possible to show all the absorption bands at their characteristic frequencies in the fingerprint region.

The FTIR has several advantages over conventional dispersive instruments: fast, sensitive MCT detectors;<sup>14</sup> high scan velocities and data collection rates; small beam size; and photometric scale accuracy. The detection of HPLC eluates can be accomplished by two methods. The first method is an off-line approach. This method involves collecting the fraction as it elutes, using the UV detector response to indicate when to collect the sample, evaporating the solvent and then making a KBr disc for a complete IR scan. The second method is direct detection via a flow cell in an on-line manner, thus avoiding possibilities of contamination, moisture uptake or other changes which might occur on collection and storage.

Two major problems concerning on-line HPLC-FTIR are regions of the spectrum blanked by solvent absorptions (opacity) and the phenomenon of solute-solvent interactions shifting solute absorption bands. These problems investigated in this study have been dealt with previously.<sup>15</sup>

Another potential problem with HPLC-FTIR is the development of a system that will separate the mixtures chromatographically without interfering with the IR detection. The solvent programming usually employed in HPLC separations results in a constantly changing background spectrum that is not easily subtracted. However, isocratic flow programming is permissible (within the pressure limits of the system) as the IR detector is insensitive to flow rate.

## EXPERIMENTAL

### Materials

The explosive mixture used in this study contained 1 mg each of nitroglycerin (NG), pentythritol tetranitrate (PETN), trinitrotoluene (TNT) and cyclotrimethylene trinitramine (RDX) in 1.0 mL chloroform (Fisher Scientific, HPLC grade). These high explosives were obtained by solvent extraction and recrystallization of military explosives using detonating cord (PETN), military TNT, and C-4 plastic explosive (RDX). The nitroglycerin was obtained from 0.6 mg Nitrostat tablets (Parke-Davis).

### Chromatograph

A Varian model 5000 chromatograph with a Valco loop-valve injector and a 3 micron Adsorbosphere column (Applied Science Labs, 10 cm x 4.6 mm) fitted with a direct-connect guard column (Applied Science Labs) and packed with 20 micron porous silica were used for all separations. All connecting tubing was 0.25 mm i.d.

The flow rate was 0.5 mL/min with a column "dead volume" of 0.4 milliliters. An isocratic 50/50 mixture of cyclohexane/methylene chloride (Fisher Scientific, HPLC grade) solvent system was used.

Two flow cells were utilized. The larger cell's dimensions were 0.2 mm pathlength and 3 mm i.d. (Nicolet Instrument Corporation). The smaller flow cell was an ultramicro cavity flow cell with a 0.05 mm pathlength and 0.2 microliter volume (Barnes Analytical). Both cells were constructed with KBr windows and low dead volume fittings.

### Spectrometer

A Nicolet 7199 FTIR with a normal KBr-Ge beam splitter was used for all infrared measurements. This spectrometer includes a laser-referenced Michelson interferometer with an absolute wavenumber accuracy specified better than  $\pm 0.01$   $\text{cm}^{-1}$ . The detector was a liquid nitrogen cooled mercury-cadmium telluride (MCT-A) detector, 7000 to 700  $\text{cm}^{-1}$ . The operating software used was supplied by the manufacturer. All data were acquired with a mirror velocity of 0.880 cm/sec and 4096 data points per scan. These conditions resulted in a constant resolution of 4  $\text{cm}^{-1}$ .

## EXPERIMENTAL RESULTS

A preliminary evaluation of the chromatographic system (*i.e.* normal or reversed phase) along with the optimized operating parameters are shown:

### CHROMATOGRAPHIC PARAMETERS

HPLC: VARIAN model 5000  
COLUMN: 3  $\mu$  ADSORBOSPHERE 10 cm x 4.6 mm (APPLIED SCIENCE)  
DETECTOR: 254 nm UV  
FLOW RATE: 0.5 ml/min  
SOLVENT SYSTEM: 50:50 METHYLENE CHLORIDE/CYCLOHEXANE  
STANDARDS: TNT, NG, PETN, RDX (1 mg/ml)  
INJECTION VOL: 30  $\mu$ l



#### NORMAL PHASE

Solvents transparent in IR region of interest  
Solvents amenable to other methods of analysis (eg) mass spec.  
Column life generally superior

#### REVERSED PHASE

Generally superior separation  
Solvents better for explosives

Retention times were 3.5 min (TNT), 6.9 min (NG), 7.0 min (PETN) and 83.5 min (RDX). The solvent composition was changed to 90% methylene chloride for RDX to speed analysis time. While this separation leaves room for improvement, it is preferable to a reversed-phase system (e.g. water and acetonitrile) due to difficulties in solvent subtraction routines in the infrared analysis.

The pure explosives were prepared for spectral analysis with KBr discs. Using a 30  $\mu$ l injection, all

compounds were chromatographed individually. The eluted species were collected, evaporated to dryness and pressed into KBr discs for spectral analysis and comparison.

On-the-fly real time measurements were investigated using Nicolet's chemigram software program. This program enables the FTIR to simultaneously monitor in real time several absorption bands. By setting the wavenumber range for each of four chromatographic windows, corresponding to each explosive, the FTIR was able to monitor and store any integrated absorbance that exceeded a preset threshold. In this manner, the chemigram produced a chromatogram similar to the UV detector output. Further, the complete IR spectra of the component was collected and stored in absorbance files for future use. A representative chemigram plot of a nitroglycerin sample (30  $\mu$ g) is shown along with its resultant on-the-fly IR spectrum.

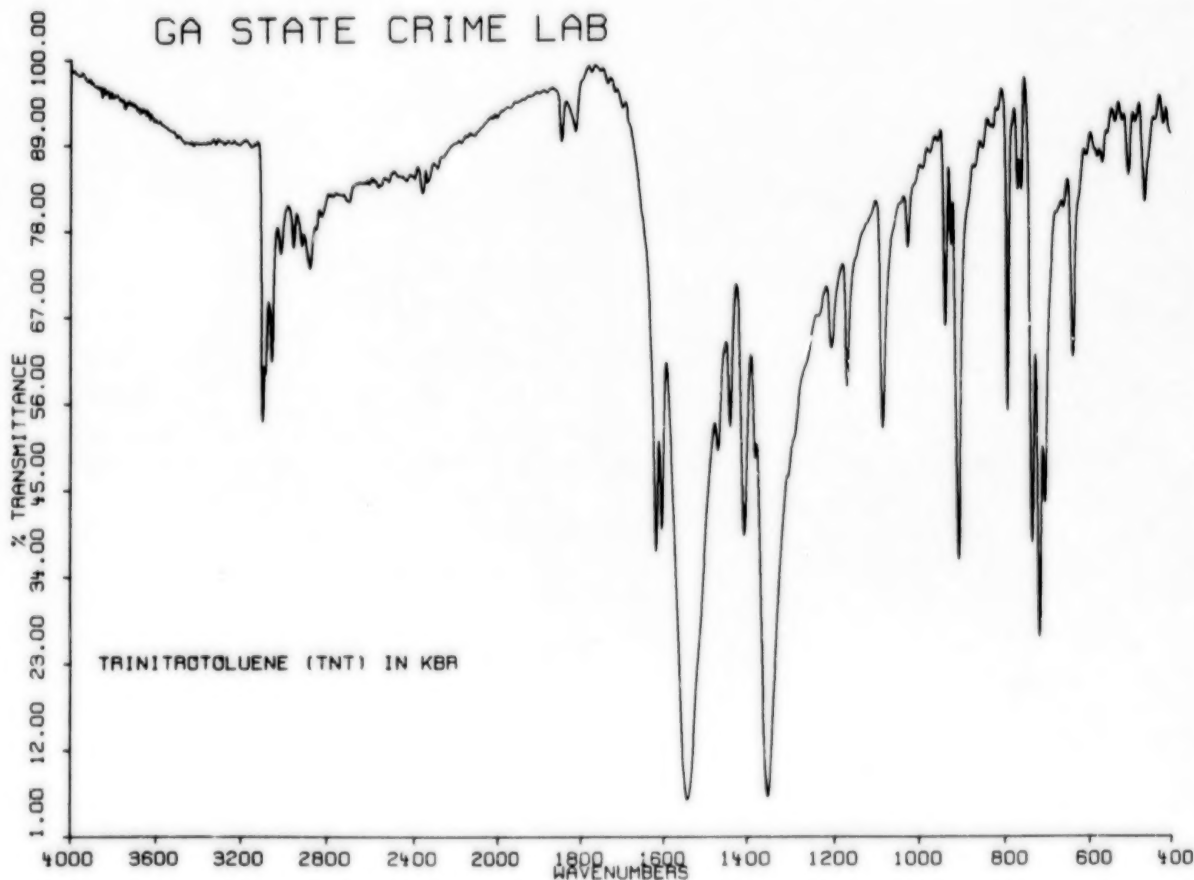


Figure 1

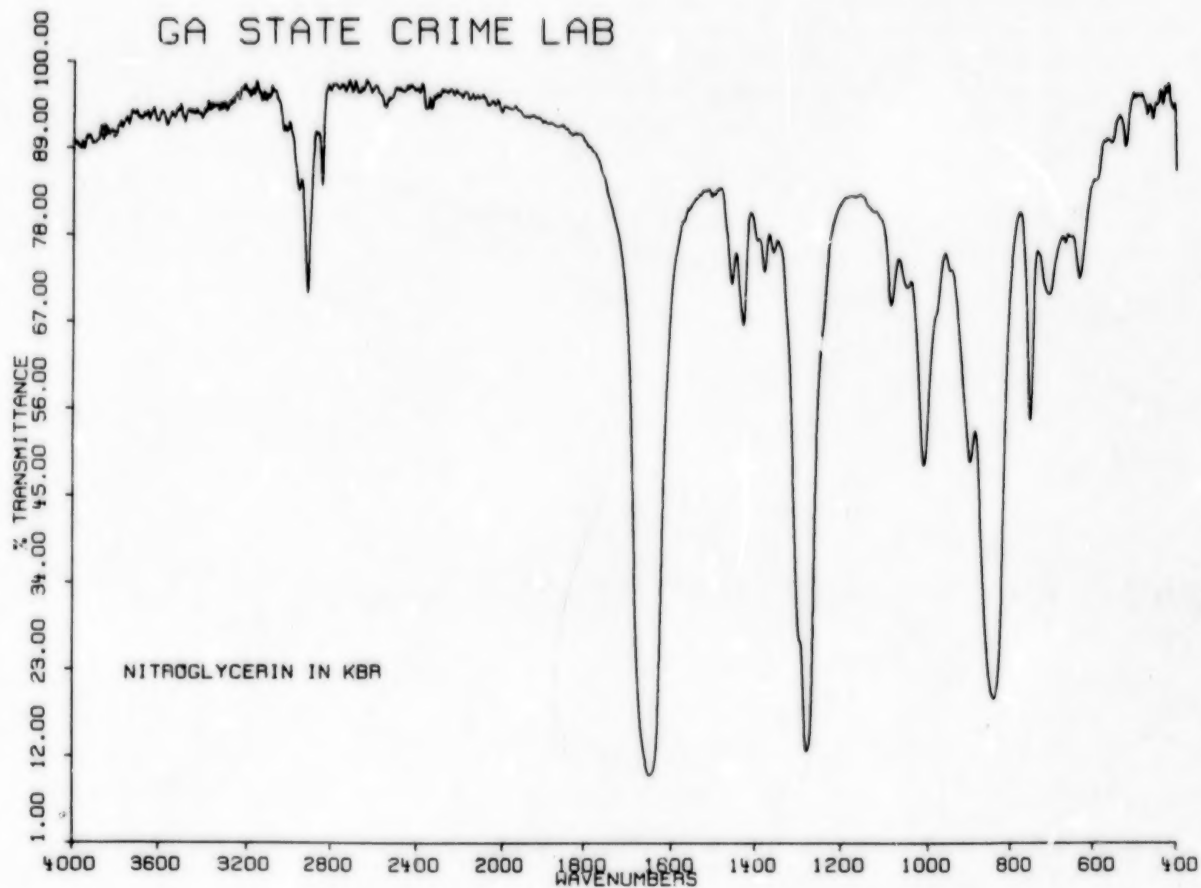


Figure 2

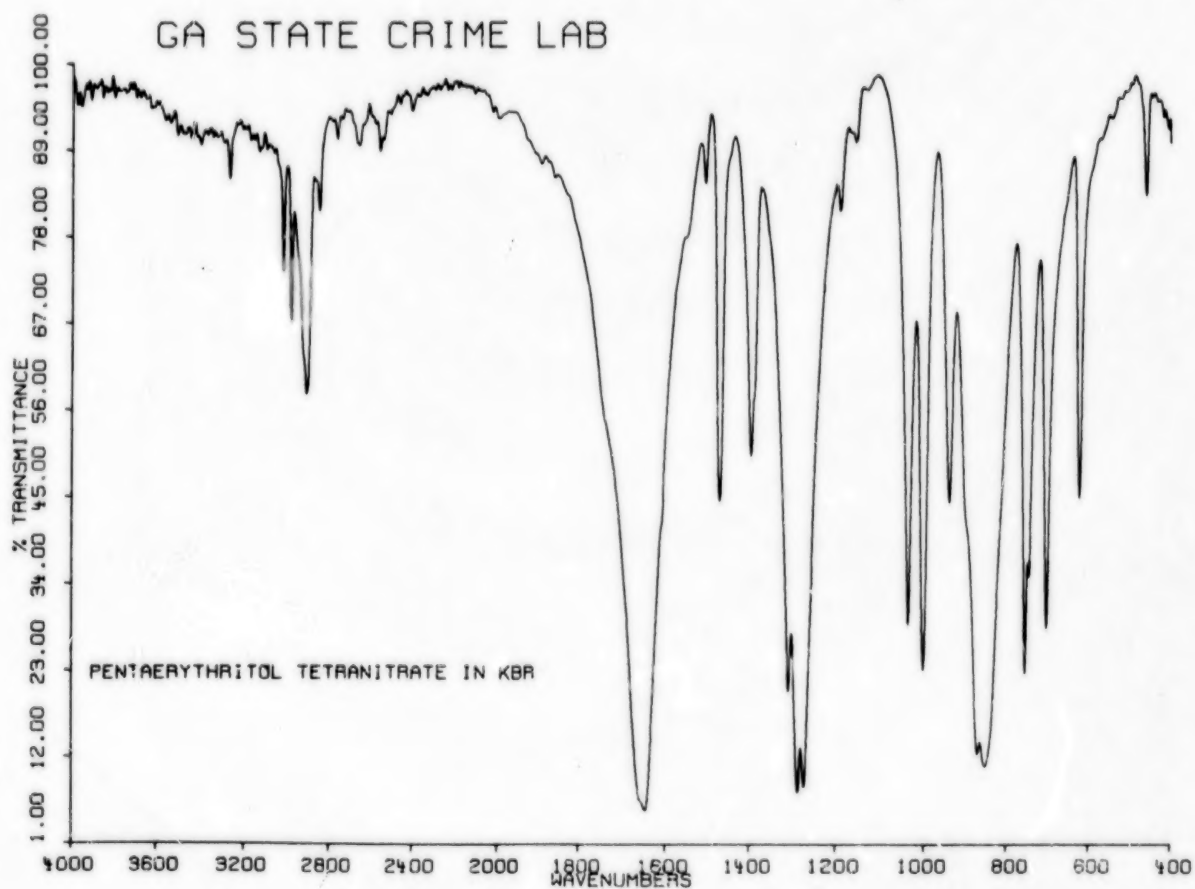


Figure 3

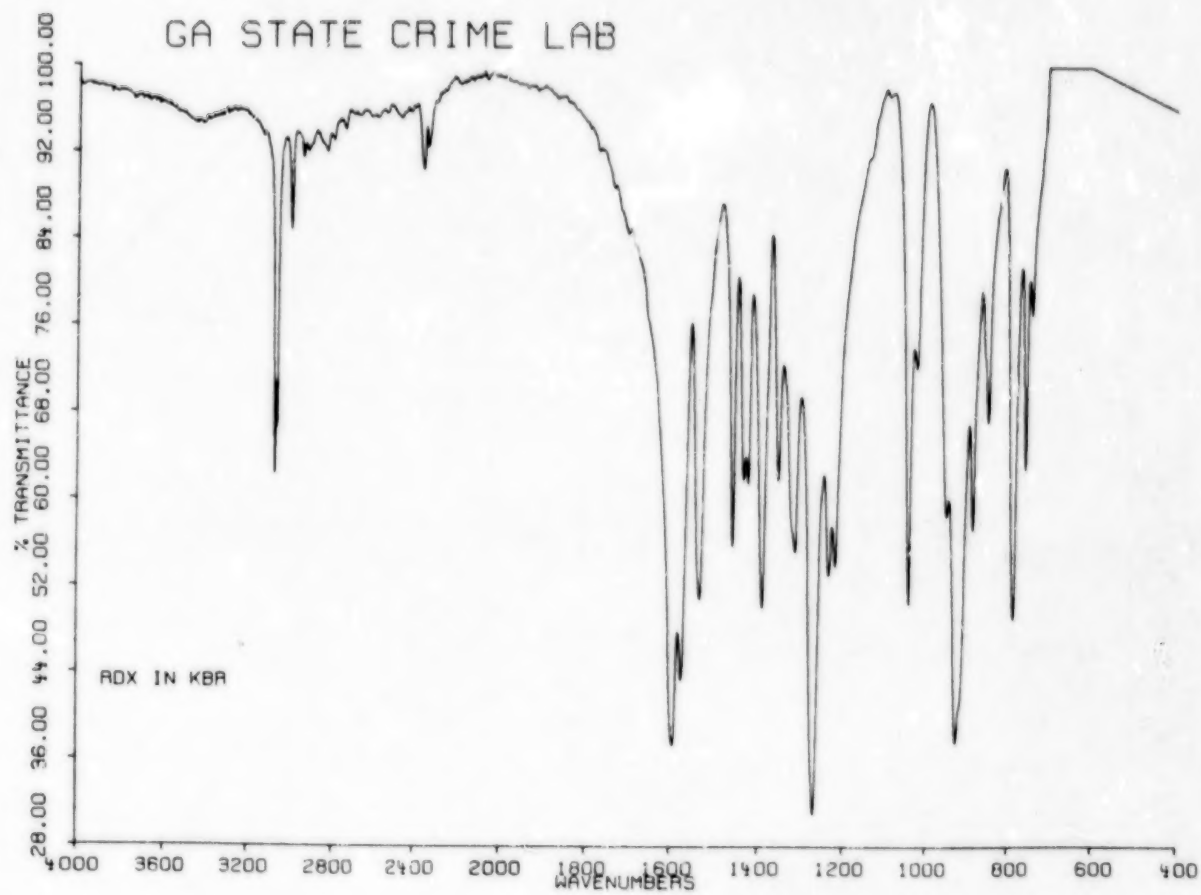


Figure 4

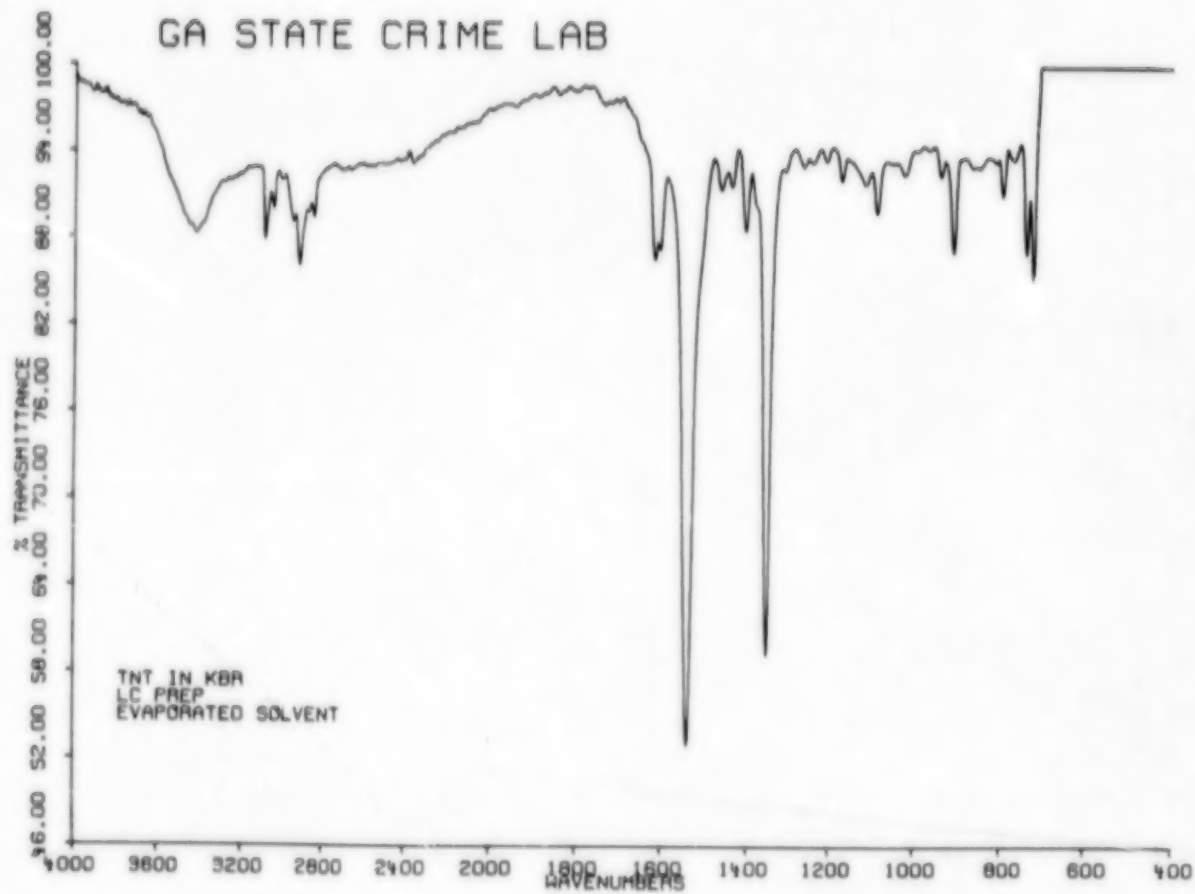


Figure 5

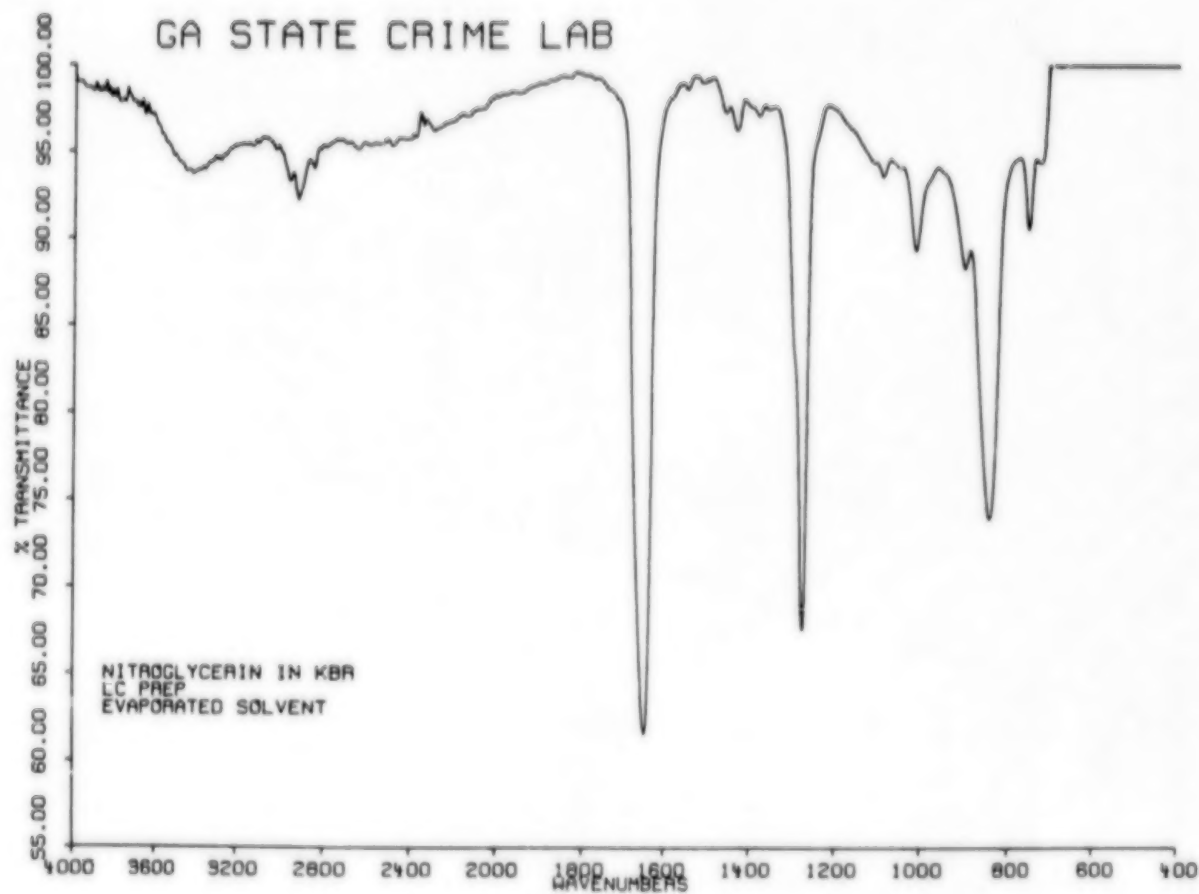


Figure 6



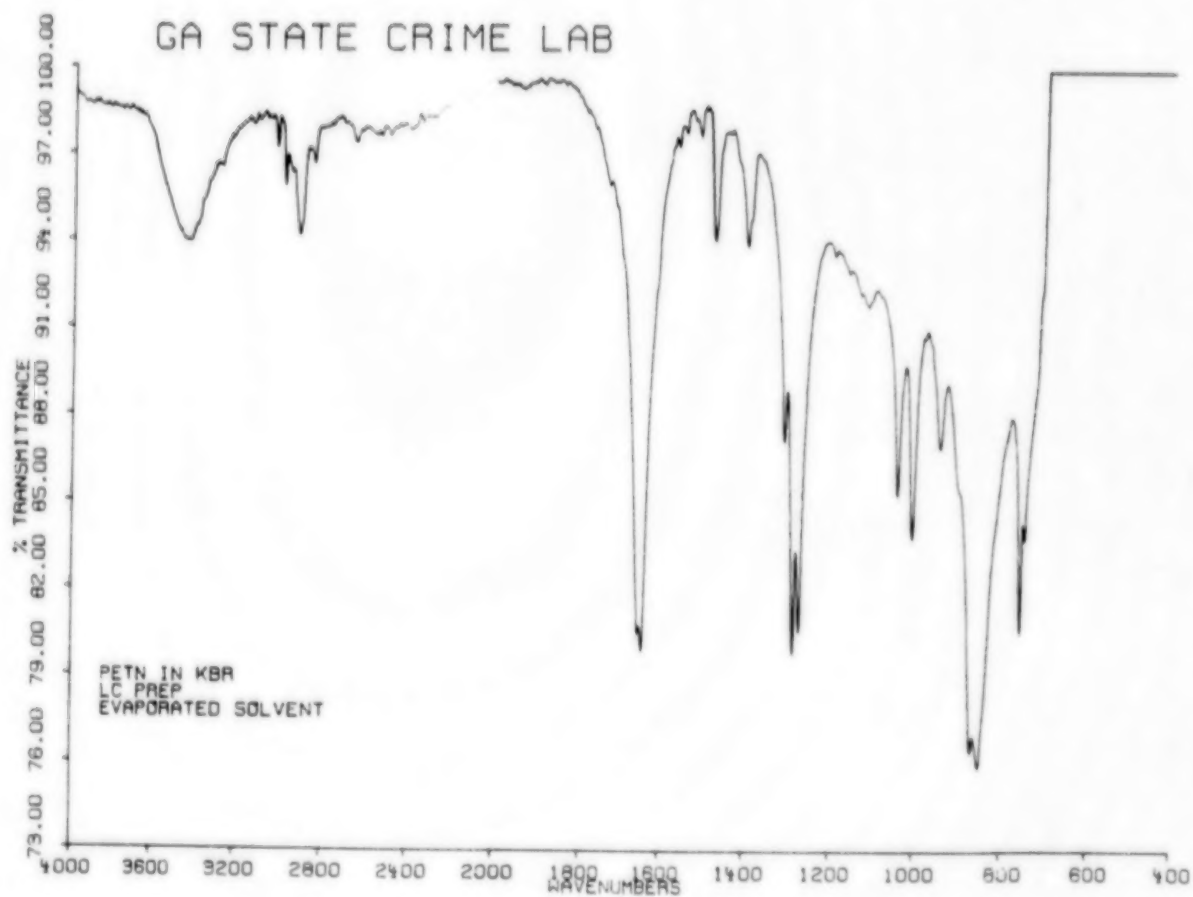


Figure 7



Figure 8

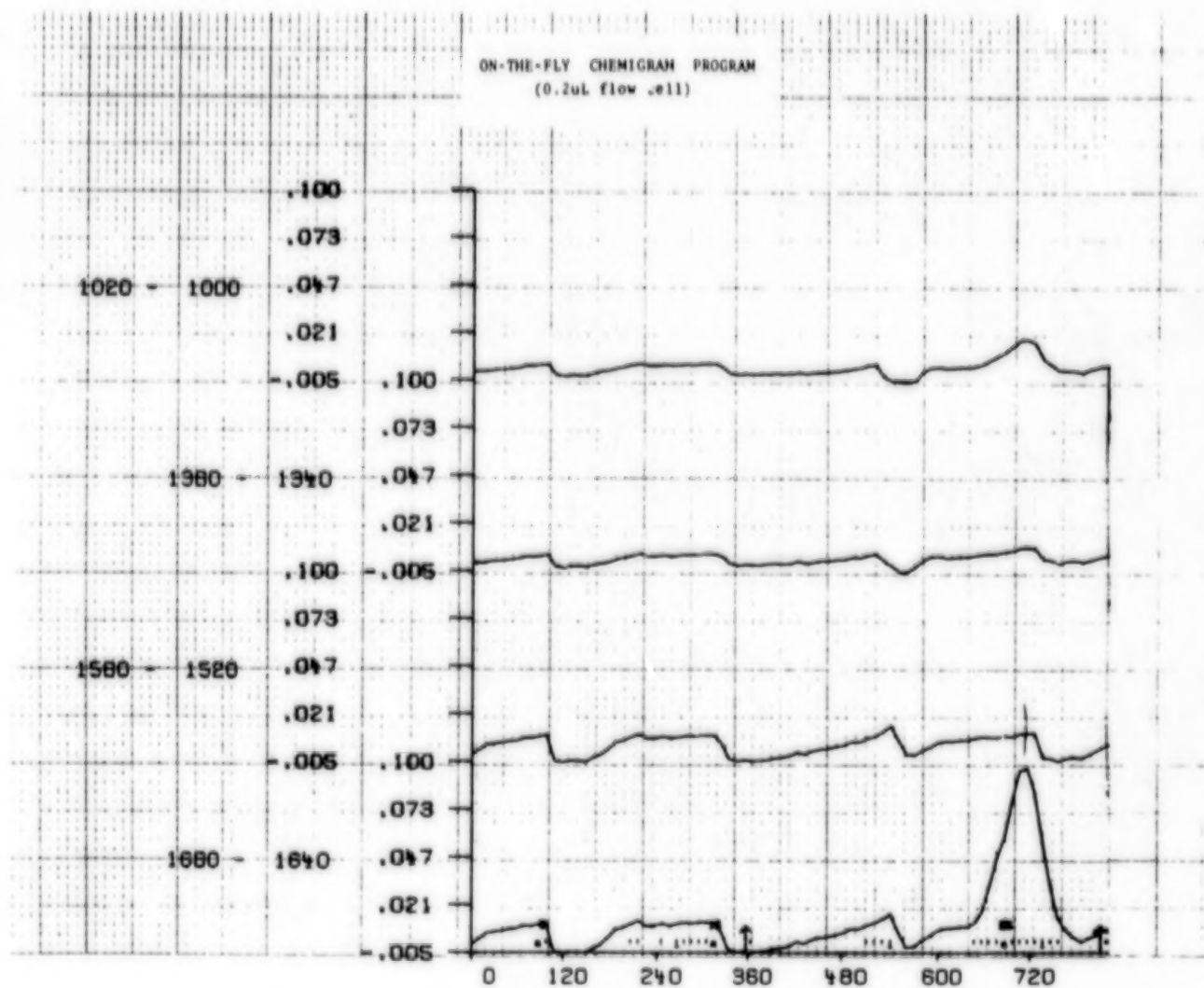


Figure 9

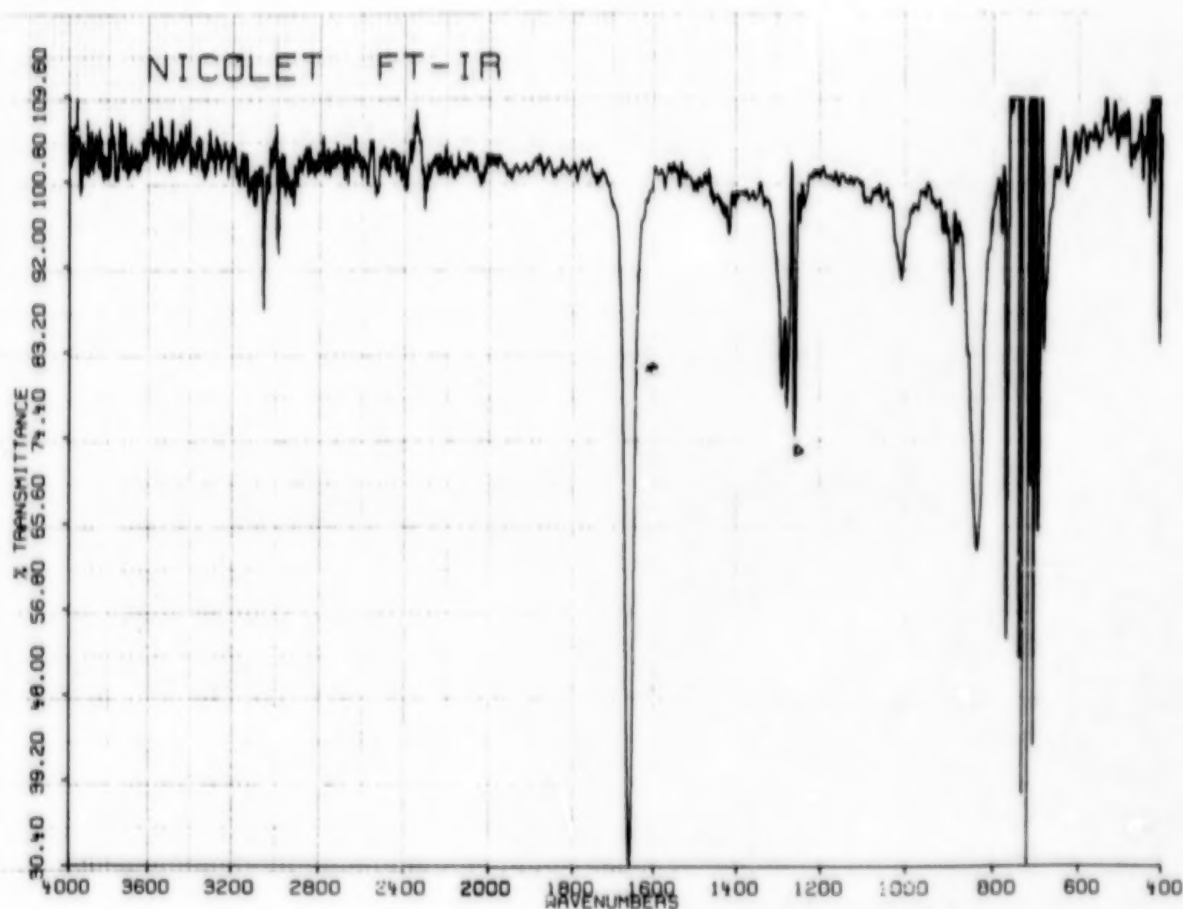


Figure 10

Each on-the-fly spectrum represents a collection of 16 scans using rapid scanning techniques (8 seconds elapsed time). This high speed scan rate permits the acquisition of a relatively large number of averaged signals in a time interval compatible with the residence time of the eluant in the flow cell.

The interval of time required for the eluant to travel from the UV detector, via the connecting tubing, to the flow cell in the IR was eleven seconds. This information enabled the development of a suitable stop-flow technique. At precisely eleven seconds after the maximum UV absorbance was observed on the HPLC recorder, the LC pump was shut off and the purge valve opened. This prevented back pressure from slowly displacing the analyte from the flow cell. At this point

1000 scans were collected, ratioed to an appropriate stored solvent background, and displayed.

Multiple runs showed this technique to be reproducible. The blank region (flat line) in each of the spectra between 700–400  $\text{cm}^{-1}$  corresponds to the cut-off region of the MCT detector. The blank region in the RDX spectra (ca. 2800  $\text{cm}^{-1}$ ) represents solvent opacity. Incomplete subtraction of solvent is also denoted by the small triangles in the stop-flow and on-the-fly spectra. Some negative deviations are also observed in the nitroglycerin spectrum due to solvent absorptions.

It was determined that the small flow cell (0.2  $\mu\text{l}$  volume) produced significantly better results than the larger volume flow cell. A background spectrum of the solvent in the ultramicro flow cell was stored for ratioing and subtraction routines.

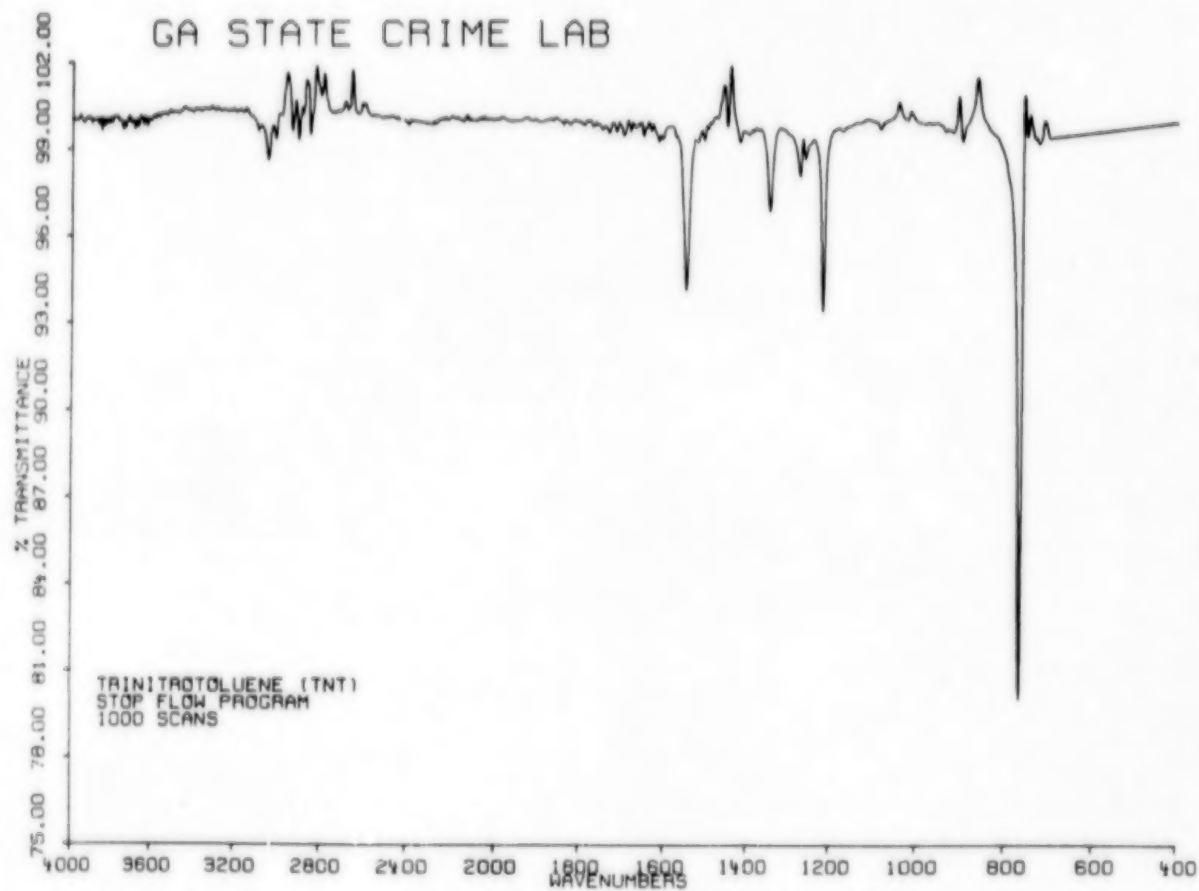


Figure 11

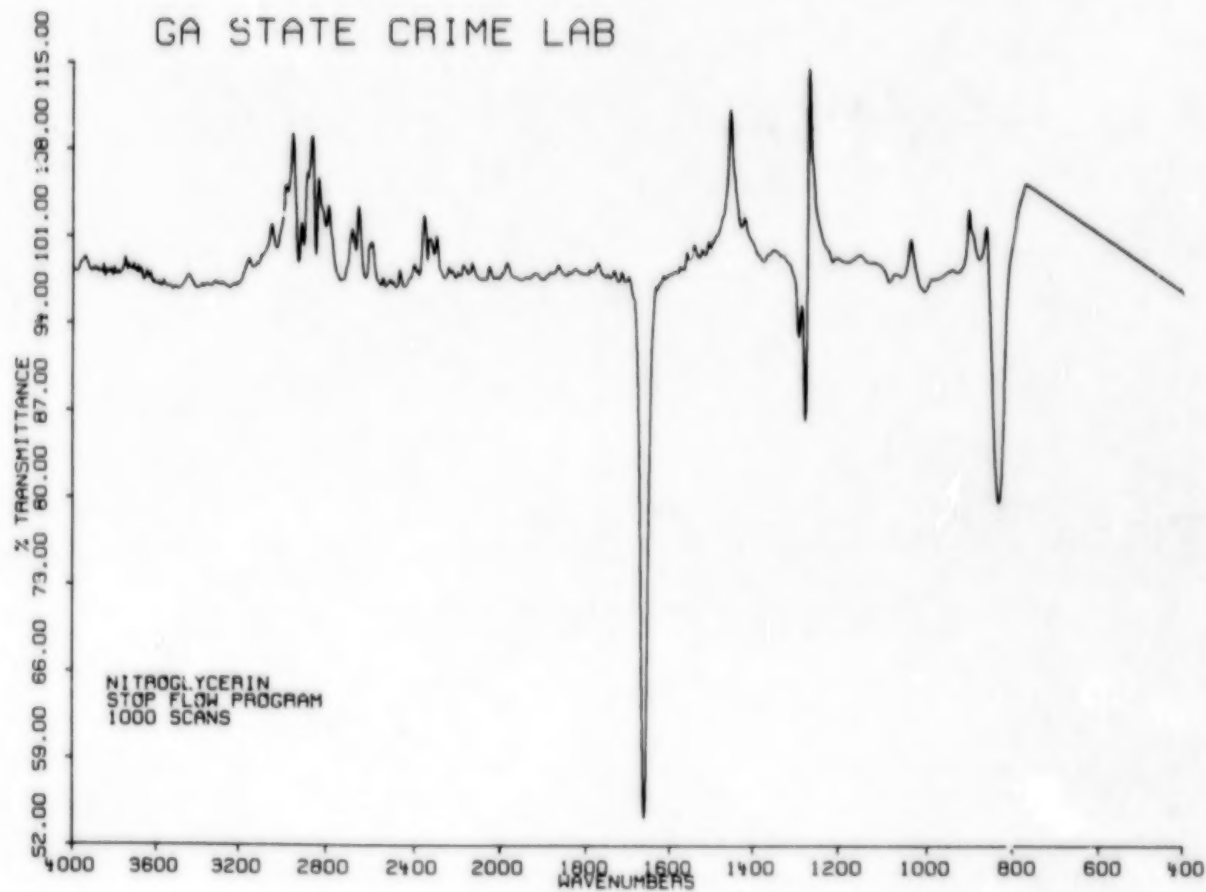


Figure 12



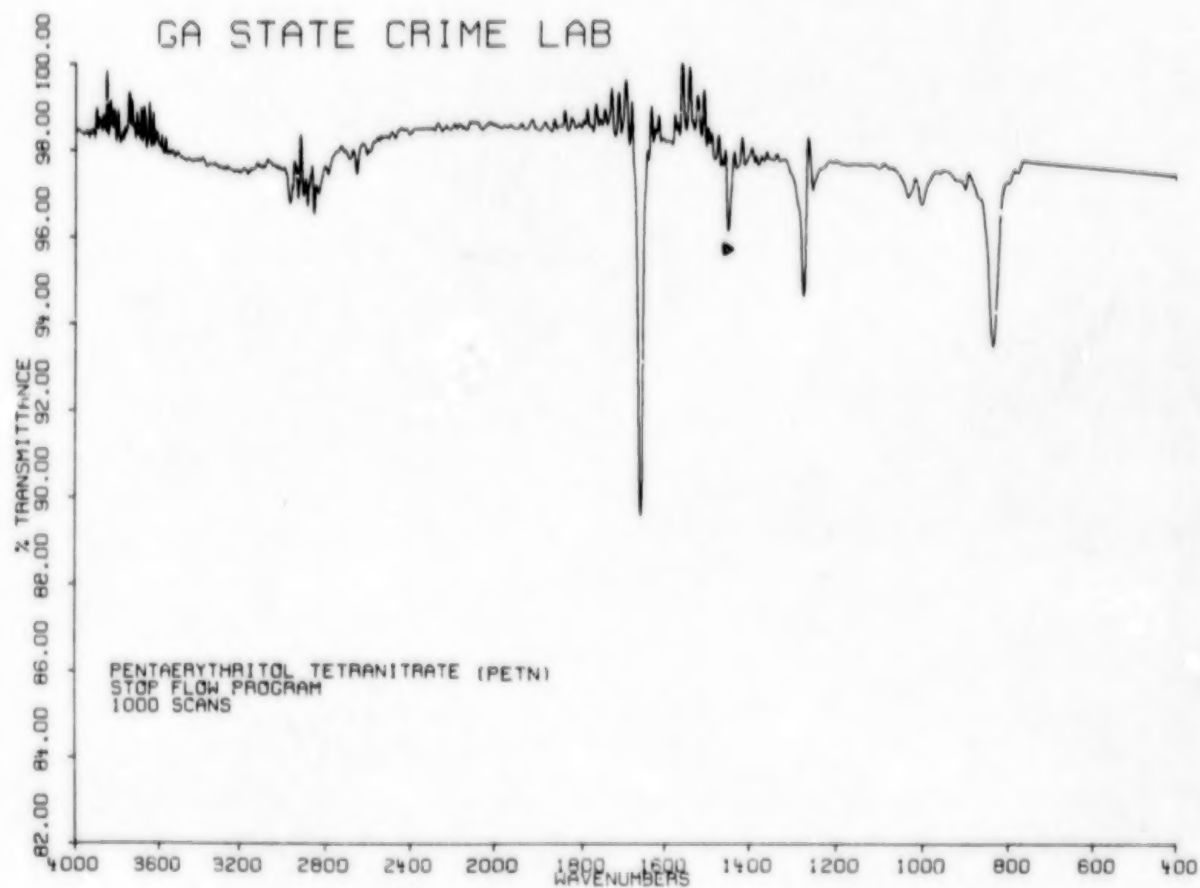


Figure 13

GA STATE CRIME LAB

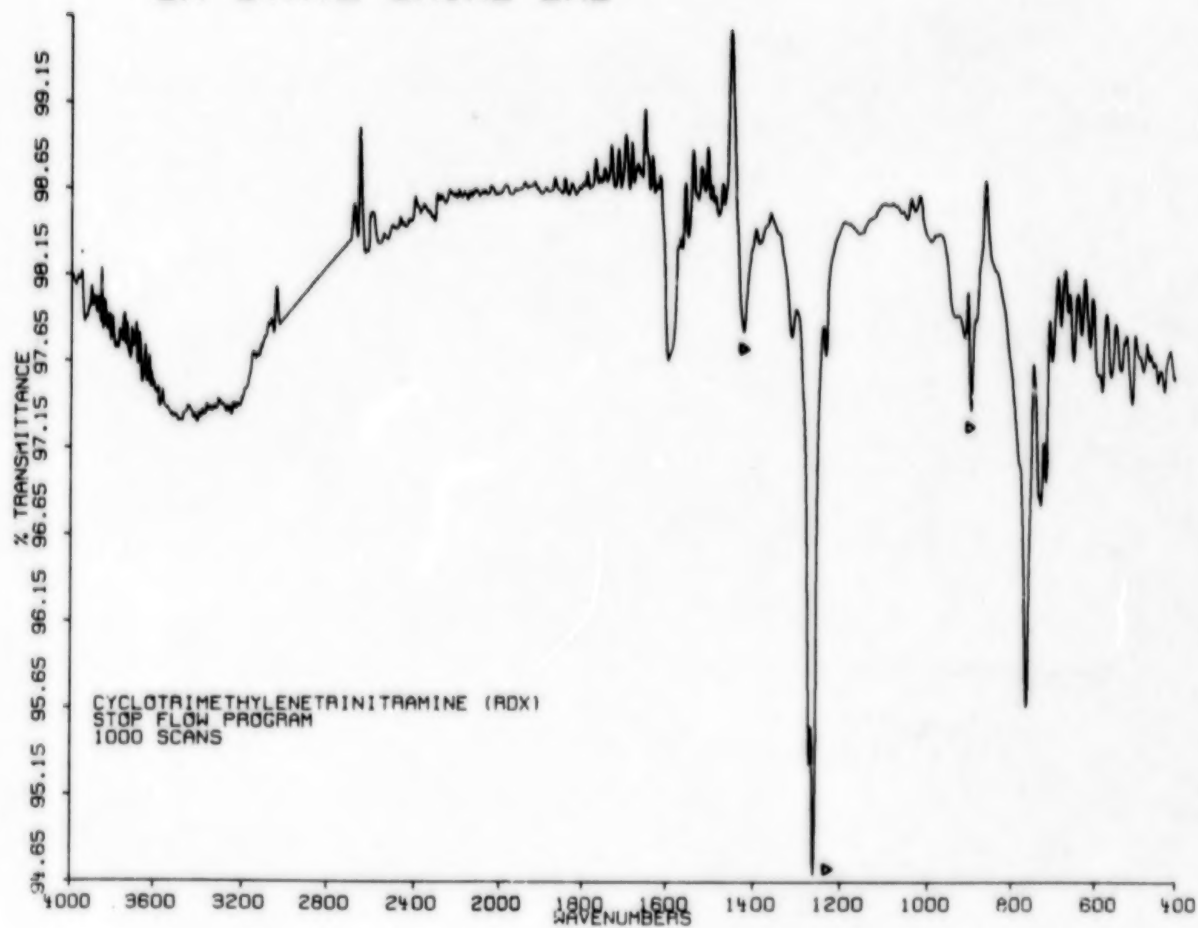


Figure 14

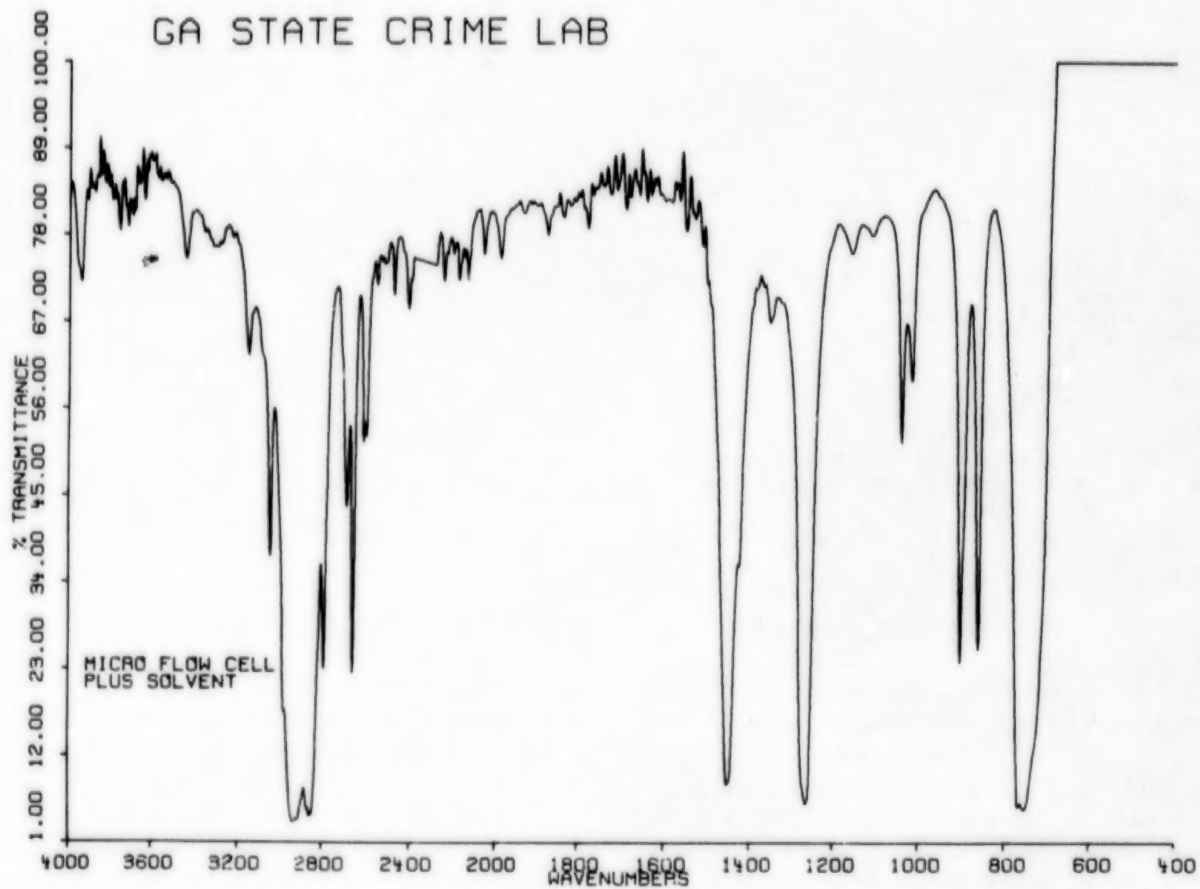


Figure 15

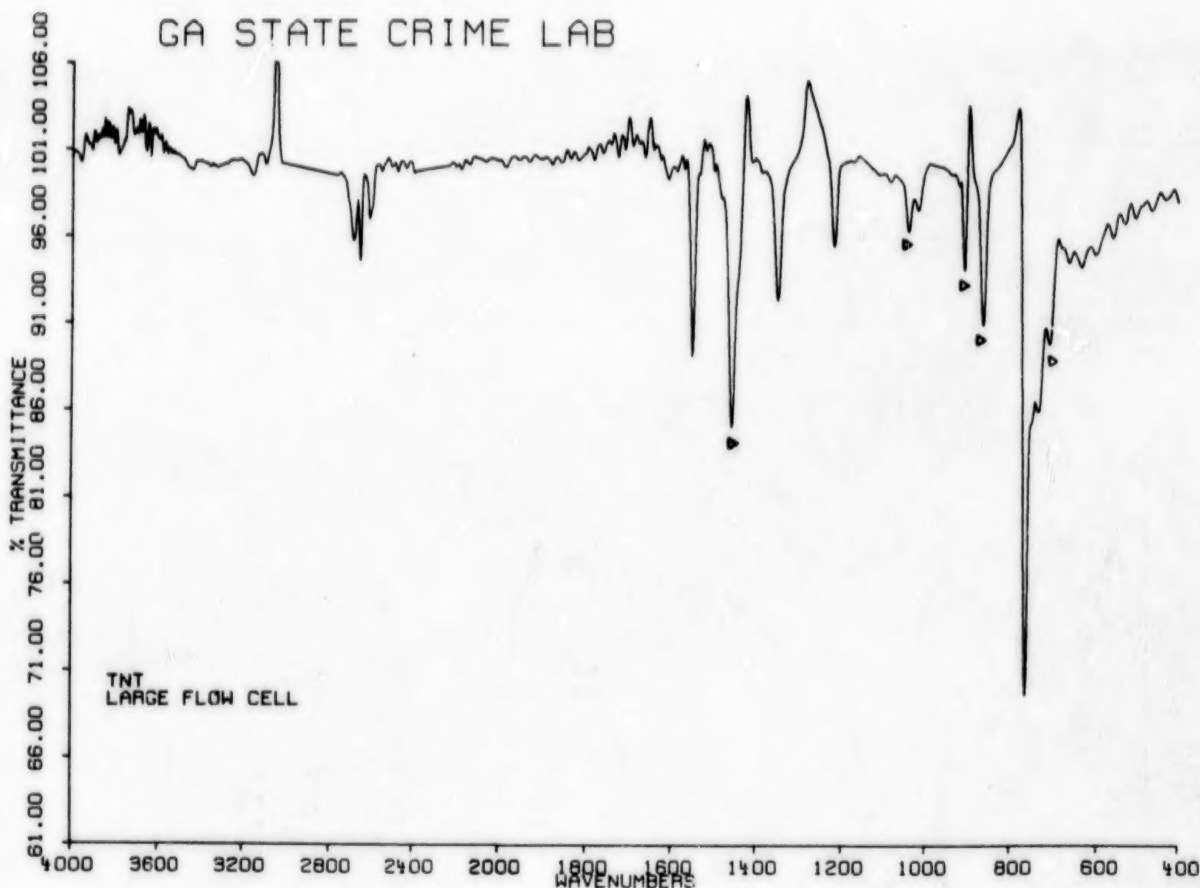


Figure 16

## DISCUSSION

The isocratic HPLC solvent system used proved to be well suited to subtraction routines. Only the N-O symmetric stretching of the nitrate esters at  $1280 \pm 10 \text{ cm}^{-1}$  was close to the solvent absorption at  $1260 \text{ cm}^{-1}$ . In general the major functional group absorbances for the explosives in this study were not affected significantly by the solvent.

Solute-solvent interactions were observed by comparing the IR spectra of the pure compound with those in dilute solution. Band shifts and band broadening appeared to be minor, approximately  $5 \text{ cm}^{-1}$ . This band shifting occurred with the similar nitrate esters. Observing the change from pure compound to the compound in solution, a doublet is clearly seen at ca.  $1290 \text{ cm}^{-1}$  for NG. The opposite effect occurs for PETN, an original triplet changing to a single band in the same wavenumber range. These effects were reproduced in consecutive analyses in this concentration range.

The solvent subtraction routines were performed by ratioing the solvent plus sample spec-

trum to solvent background spectrum. Perfect ratioing is only possible if no interactions occur between the two. This method is theoretically correct for dilute solutions. At high solute concentrations a slight negative spectrum was observed representing displacement of solvent by the sample. The attempt to minimize this displacement by increasing the solvent size proved to make the subtraction less effective.

Detection limits were not an objective of this study and would depend on the molar absorptivity of the analyte along with the chromatographic peak volume. The working amount of explosive detected was  $30 \mu\text{g}$  which should be the approximate sample weight in the flow cell. With more dilute solutions an order of magnitude in sensitivity should be attainable by increasing the number of scans and optimizing the sharpness of the chromatographic elution band. The faster, more sensitive MCT detector used in this study is a necessity since the conventional TGS room-temperature detector showed insufficient sensitivity in this investigation.

## CONCLUSIONS

This HPLC-FTIR system permits on-the-fly real time measurements in flow cells thin enough to overcome solvent opacity in the analysis of relatively concentrated solutions. For more dilute solutions, such as traces of explosives, the use of the stop-flow method to obtain a complete IR spectrum is superior. This technique of using and/or identifying characteristic molecular frequencies at a particular chromatographic retention time enables the forensic chemist to make a complete identification of the explosive.

Further developments in this laboratory with this system hopefully will include optimizing detection to sub-microgram levels. Improvements are needed in the separation and identification of NG and PETN. Indexing the UV absorbance to the IR absorbance at a characteristic wavelength should increase the specificity of this method.

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## ANALYSIS OF SMOKELESS POWDERS USING UV/TEA DETECTION

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**ABSTRACT.** The analysis of smokeless powders or propellants have been of long interest to the forensic examiner. Smokeless powders contain not only explosives such as nitroglycerine and nitrocellulose but also stabilizers gelatinizers and their various decomposition products which are themally labile. High Performance Liquid Chromatography allows their accurate characterization and quantitation. By using tandem UV/TEA detectors these compounds can be analyzed in the low nanogram range which is a requirement for some forensic applications. Diphenylamine, 2-nitrodiphenylamine, N-nitrosodiphenylamine, nitroglycerine, 2,6-dinitrotoluene and 2,4-dinitrotoluene have been separated identified and their relative quantites used to characterize the gun powder.

### INTRODUCTION

Smokeless powders consist mainly of nitrocellulose. The burning rate of the propellants are adjusted by varying the size and shape (ball, disk, cylinder), or by the addition of chemical modifiers and stabilizers. These compounds are what are of interest here. Gunpowders are grouped into three basic categories—single, double, and triple base. Single base powders consist mainly of nitrocellulose (NC). The addition of nitroglycerin (NG) to the nitrocellulose makes the propellant double base. A powder containing NG, NC and nitroguanidine salts is classified as triple base. These are used in rockets and military ordinance.

Seven major constituents of smokeless powder were separated and identified. They are diphenylamine (DPA), 2-nitrodiphenylamine, 2,6 dinitrotoluene, 2,4 dinitrotoluene (DNT), nitroglycerin, N-nitrosodiphenylamine and n-butylphthalate. Diphenylamine and 2-nitrodiphenylamine are added to the nitrocellulose to stabilize it. They scavenge the nitric (nitrous) acid which is formed during the decomposition of NC. In turn the diphenylamines are nitrated and nitrosated (N-nitroso DPA). 2,4 DNT and its impurity 2,6 DNT are added to the propellant to modify the surface. The explosive oils, notably NG serve two functions — to increase the burning rate, and as a plasticizer or gelatinizer for the nitrocellulose. Dibutyl phthalate serves the latter purpose.

The ultraviolet (UV) detector provided sensitivity in the nanogram range for the compounds con-

taining the aromatic moiety, but was less specific to the nitrate esters (NG). The Thermal Energy Analyzer (TEA) on the other hand was selective for nitroglycerin and N-nitroso DPA. The aromatic nitro compounds showed poor sensitivity on the TEA because the 550°C pyrolysis temperature is not enough to effectively cleave the carbon-nitrogen bond.

In pre-blast situations or when comparing powders for a possible common origin, the analysis is straightforward. An association with the manufacturer and brand can usually be made if you have the standards. Post blast identification of powders is generally more difficult and sometimes impossible. After ignition or upon exposure to heat the smokeless powders shrink or melt, altering their chemistry significantly. Also introduced into the sample are various contaminants ie. pyrolysis products, oils, plasticizers, and building materials. In this case strict quantitation which is essential in discriminating some brands is impossible. The analysis must be focused on identifying components unique to specific types of powders. This is where the TEA proves valuable.

### EXPERIMENTAL PROCEDURE

Ten grains of each powder were extracted with five milliliters of methylene chloride. The extract was then passed through a silica Sep Pak followed by five milliliters of fresh solvent. The solution was then evaporated to half its volume with a ni-

trogen stream. This solution was then injected into the HPLC.

The HPLC system consisted of two Waters 6000A pumps and a U6K injector fitted with a 10  $\mu$ l loop. A Kratos 770 variable wavelength detector in line with a Thermal energy analyzer, manu-

factured by Thermal Electron were used to monitor the eluting stream. The UV detector was set at 254nm. and a pyrolysis temperature of 550°C was maintained on the TEA. The eluent was seventy percent isoostance in methylene chloride at a flow rate of two milliliters per minute.

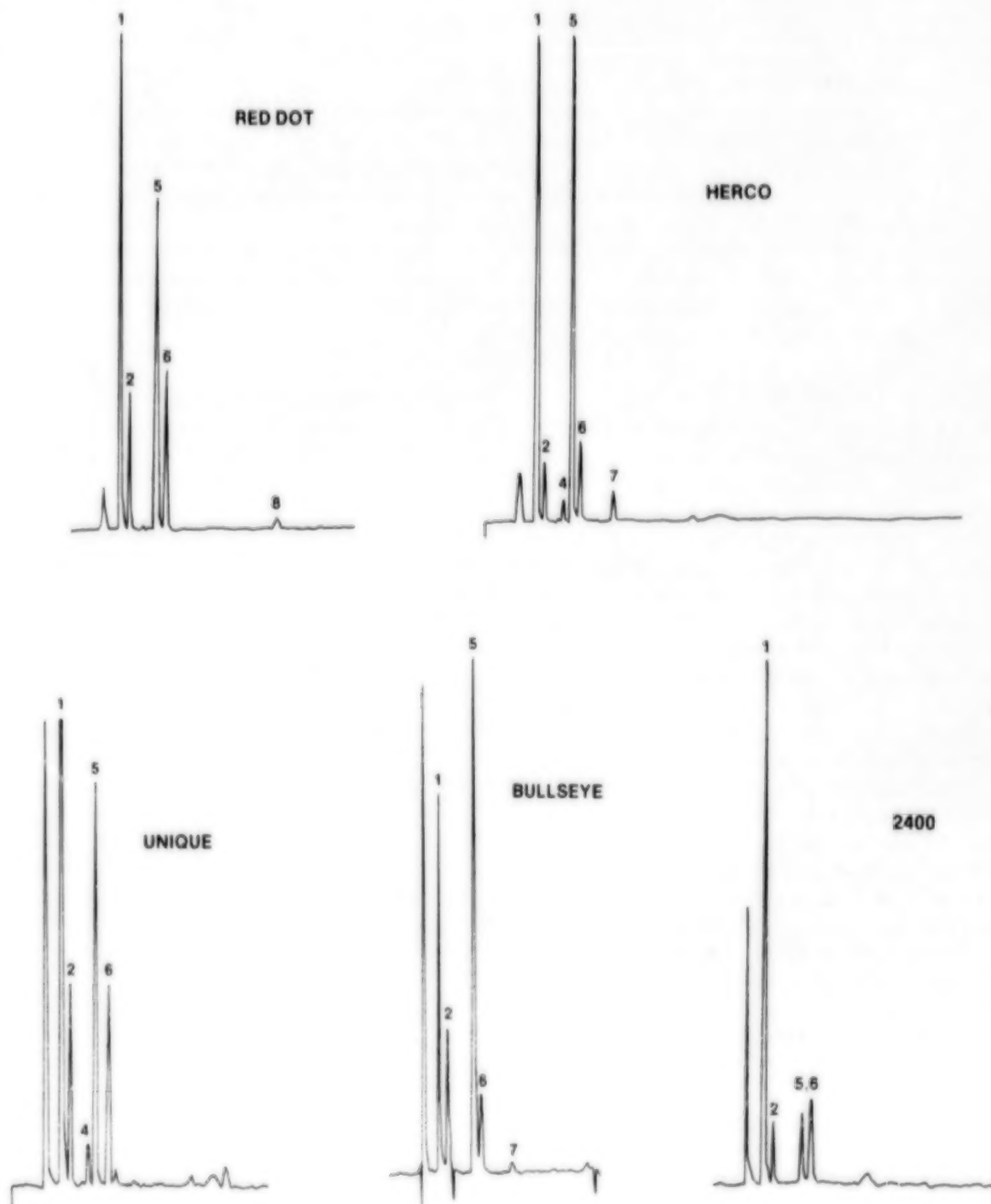


Figure 1. UV response Hercules disk powders 1. DPA, 2. 2-nitro DPA, 3. 2,6 DNT, 4. 2,4DNT 5. NG, 6. N-nitroso DPA, 7. Unknown, 8. DBP

The first propellants analyzed were disk shaped powders from the Hercules Powder Company. (Figure 1) They were Red Dot, Herco, Unique, Bullseye and 2400. Their are similarities in the Hercules line notably the presence of the four compounds DPA, 2-nitro DPA, NG, N-nitroso DPA. Only two contain 2,4 DNT (Herco,

Unique). The relative quantities of the major components and the presence or absence of minor components allow the easy discrimination of each of these powders. The TEA responded only to nitroglycerin and the n-nitrosodiphenylamine and added little information to the UV chromatogram (See Figure 2). Physical diameter, thickness, and

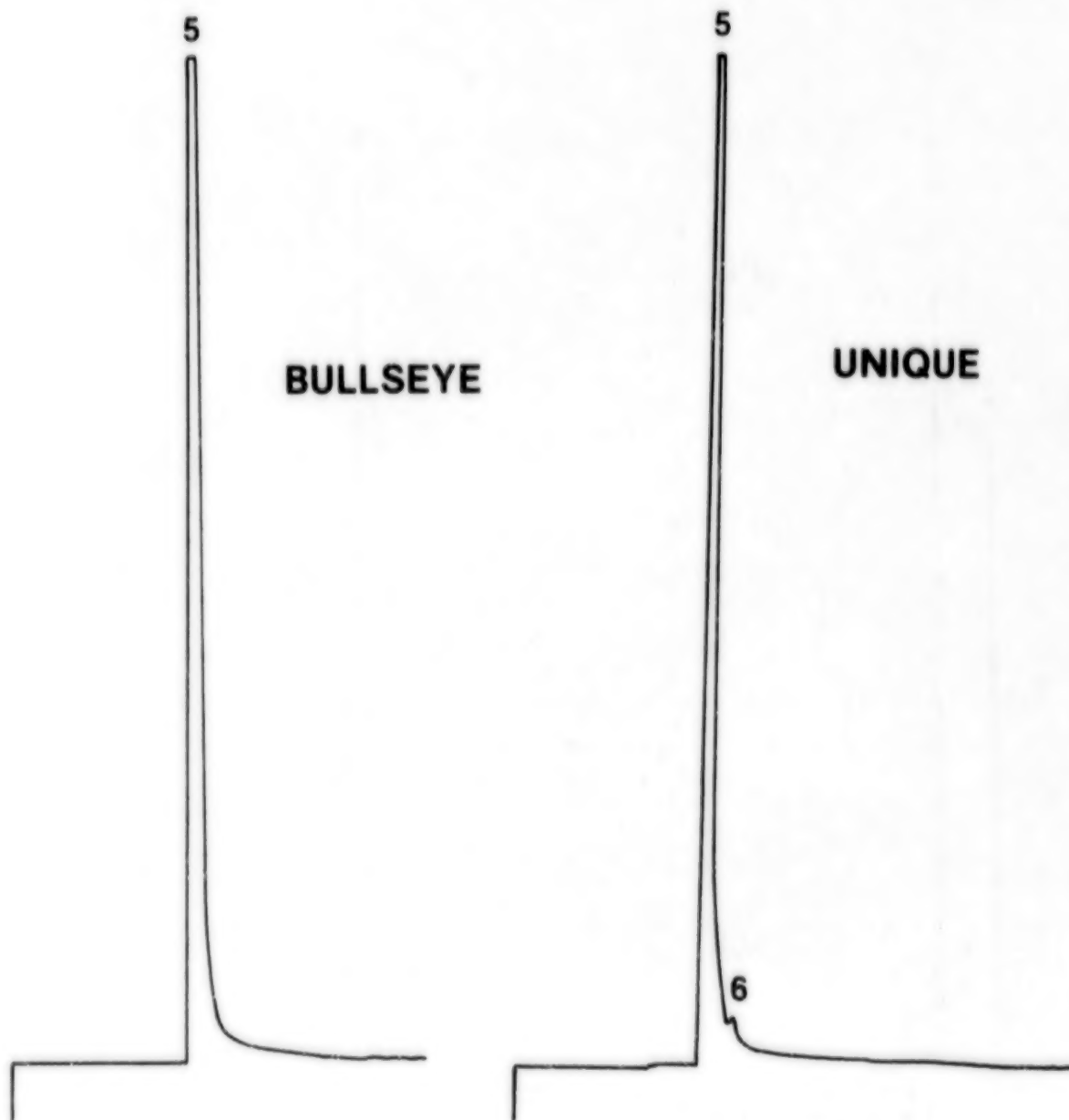


Figure 2. TEA response Hercules disk powders 5. NG, 6. N-nitroso DPA

the perforation or lack of perforations will add further clarification to the identity of the powder. It should be noted that all the Hercules flake powders are double-base; this is not the case for other manufacturers.

The disk powders in the Dupont series varied greatly. The propellant designated "PB" proved to be single-base with large amounts of 2,4 DNT and DPA. (see Figure 3). The TEA showed the absence of NG with only N-nitrosodiphenylamine

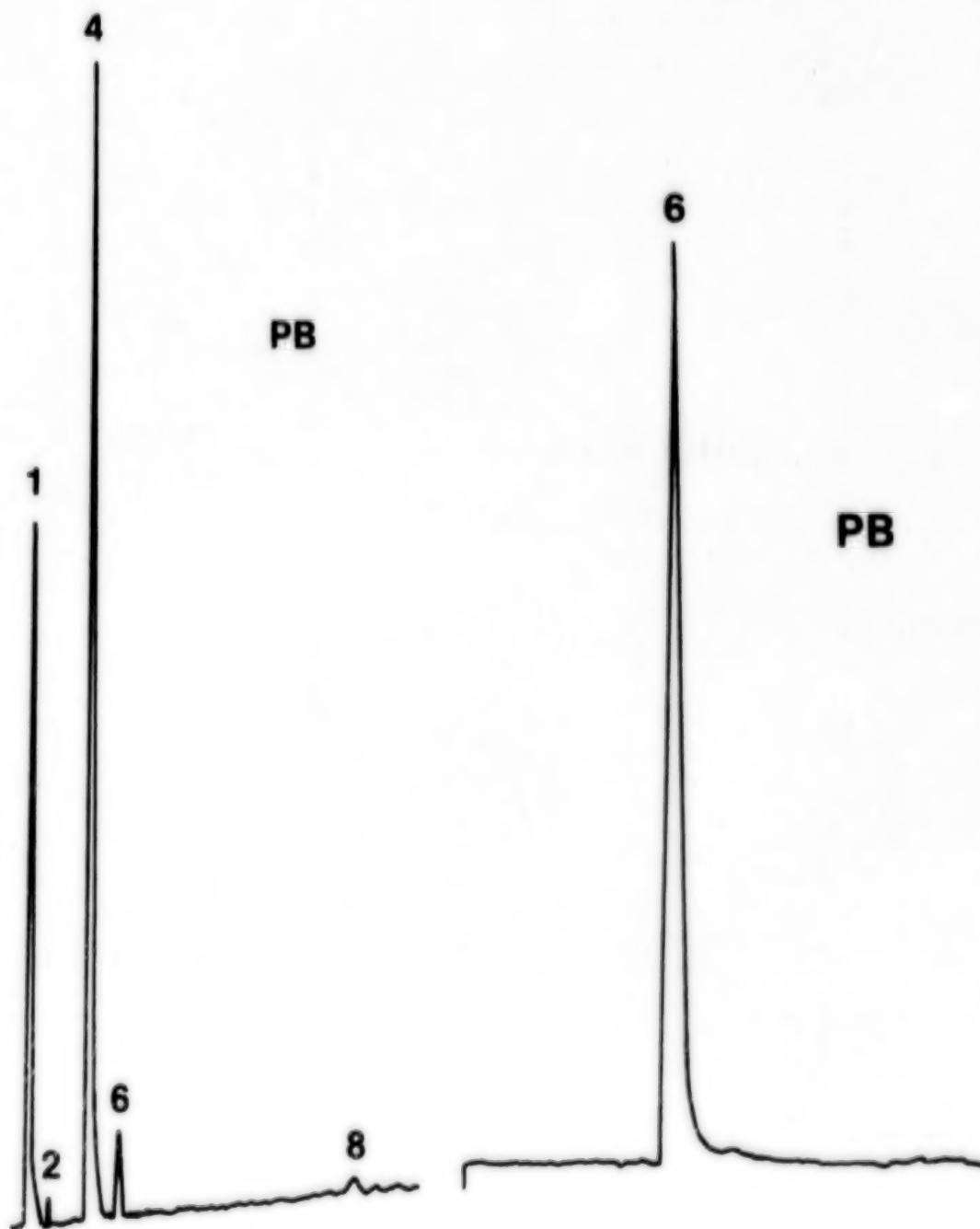


Figure 3. Dupont disk powder 1. 1. DPA, 2. 2-nitro DPA, 4. 2,4 DNT, 6. N-nitroso DPA, 8. DPA

appearing in the chromatogram. Conversely Dupont 700-X was shown to be double-base. It also showed an abundance of 2,4 DNT and DPA but had a significant amount of NG. (see Figure 4). It was later shown that the "X" designation in a Du-

pont powder indicates the presence of NG. Also large amounts of 2,4 DNT in a disk shaped powder would be significant in discerning a Hercules from a Dupont propellant.

Two other flaked powders were examined—

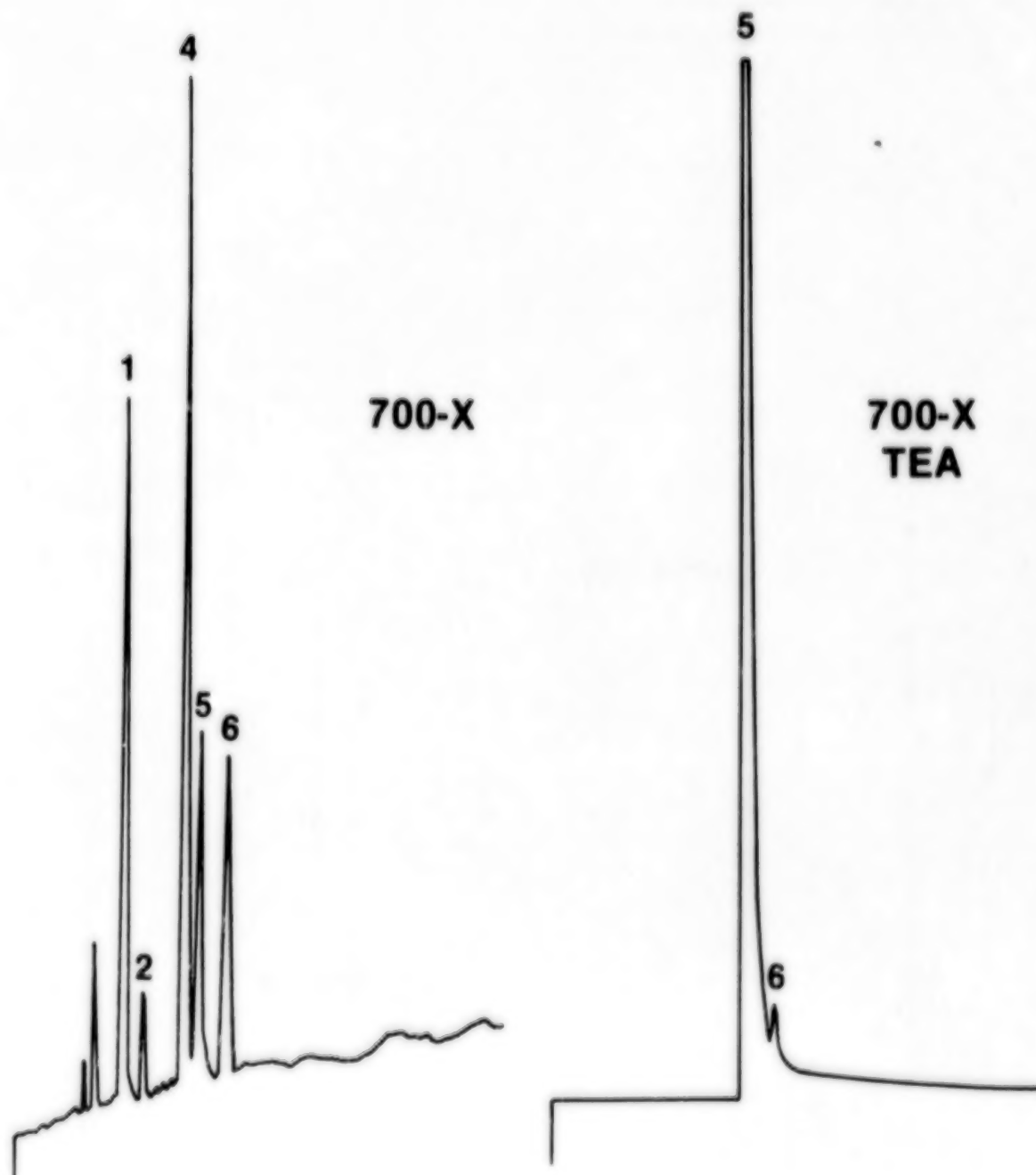


Figure 4. Dupont disk powder 1. DPA, 2. 2-nitro DPA, 4. 2,4 DNT, 5. NG, 6. N-nitroso DPA

Nike and Norma 2020. The Nike powder was shown to be double-base. It contained DPA, 2-nitro DPA and a large amount of N-nitroso-DPA. (Figure 5). This is probably due to the age of the powder. Most of the DPA originally present has decomposed to its nitroso derivative. The Norma powder showed only NG present in significant amounts.

The ball powders are exclusively double base. Physically they appear as small balls, flattened balls or a mixture of both. Examples of ball powders are two manufactured for the Hodgdon Powder company—H-110 and H-BLC-2. These pow-

ders contain the same components the differences being in their relative quantities. The greatest disparity in the brands lies in the large amount of the unknown compound at retention time 23.07 in H-BLC-2 and a considerably smaller amount in H-110. (see Figure 6). Another ball powder Winchester Western WW-296 is very similar to the Hodgden powders (Figure 7). Winchester Western 252-AA shows the presence of a large amount of an unknown compound at retention time 26.6 which distinguishes the AA powders from all others.

The Dupont IMR (improved military rifle) sin-

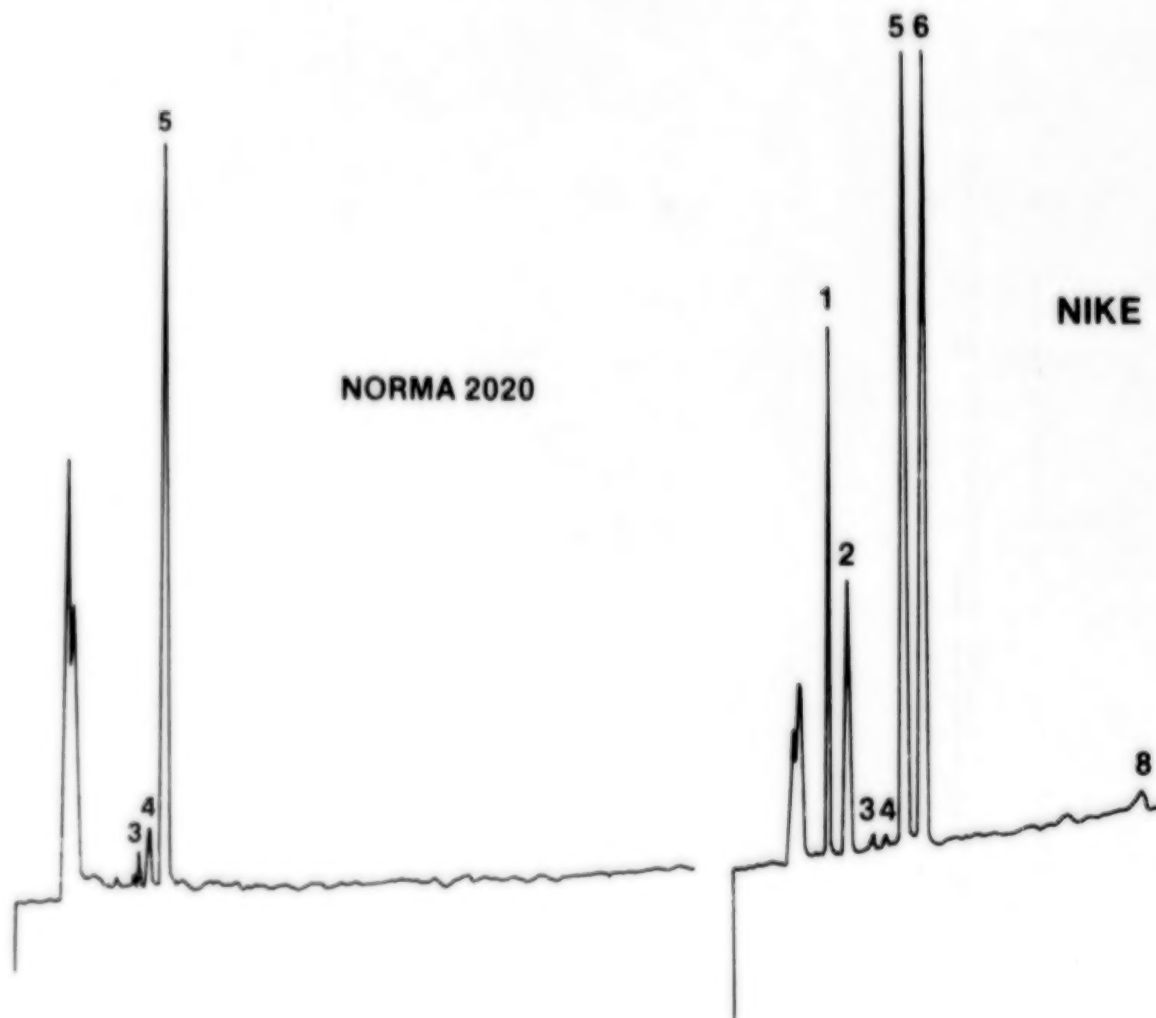


Figure 5. UV response Nike and Norma disk powder 1. DPA, 2. 2-nitro DPA, 3. 2,6 DNT, 4. 2,4 DNT, 5. NG, 6. N-nitroso DPA, 8. DBP



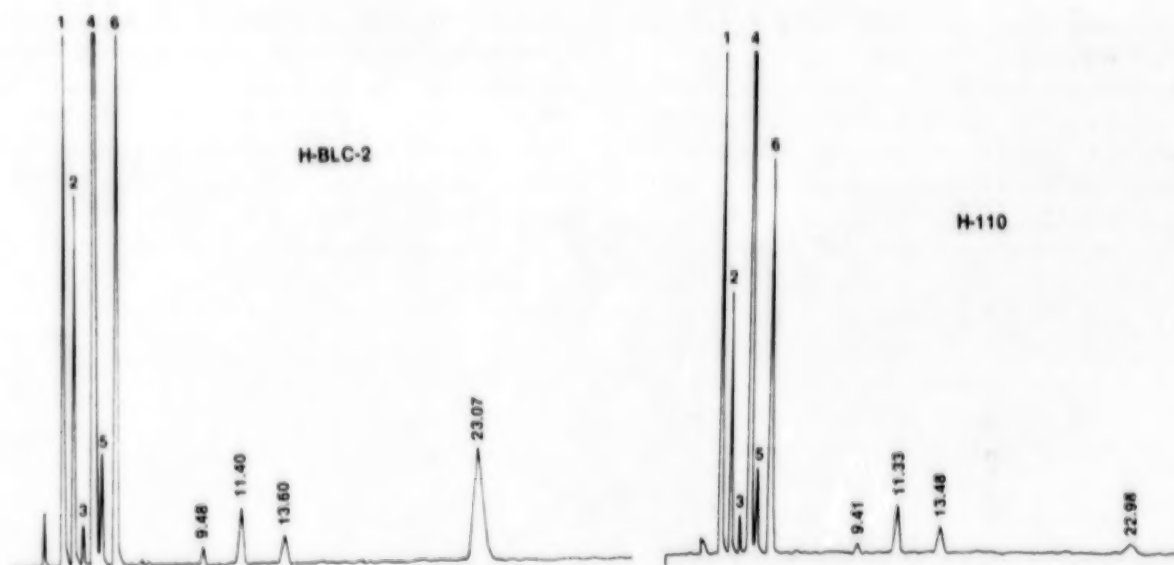


Figure 6. UV response Hogdon ball powders 1. DPA, 2. 2-nitro DPA, 3. 2,6 DNT, 4. 2,4DNT, 5. NG, 6. N-nitroso DPA

gle base series is typified by the large amount of 2,4 DNT. (Figure 8). Present in small quantities are DPA, 2-nitro DPA, the 2,4 impurity 2,6 DNT, N-Nitroso DPA and n-butyl phthalate. The relative ratios of these lesser components prove to be the key in distinguishing chemically the members of the IMR series. (measuring the length of the cylinder is a more definitive tech-

nique if the powder is intact). The TEA shows a large response for the nitrosamine and gives a small peak for 2,6 DNT. Herter's 100 another cylindrical single base powder shows large amounts of DPA and very little 2,4 DNT contrary to the IMR series. (Figure 9) The TEA shows again a large response to N-nitroso DPA but another compound of unknown identity is revealed.

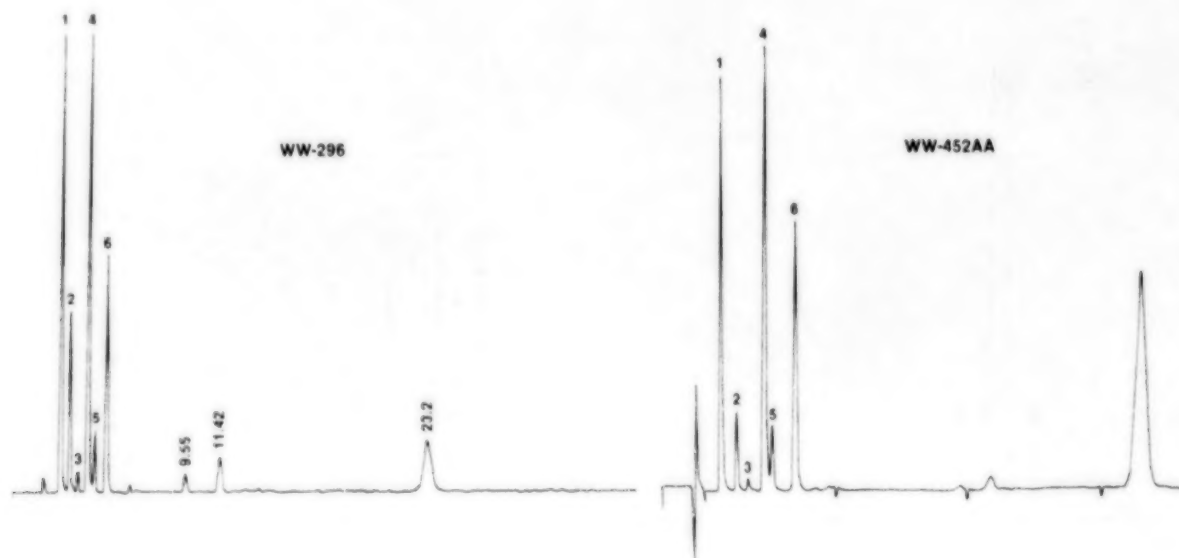


Figure 7. UV response Winchester Western 296 and 252AA 1. DPA, 2. 2-nitro DPA, 3. 2,6DNT, 4. 2,4 DNT, 5. NG, 6. N-nitroso DPA

As was shown most cylindrical propellants are single base, there is however, a notable exception the Hercules Reloader line. For example, RL-7 contains DPA and its decomposition product, N-Nitroso-DPA lesser quantities of 2-nitro DPA and 2,4 DNT but is also has NG, making it double base. The TEA chromatogram shows NG, the nitrosoamine plus what is apparently EGDN.

In order to study post blast propellants pipe bombs were constructed. They were initiated with safety fuze. The pipe fragments were collected and were brushed off to remove any residual powder. The fragments were then extracted with dichloromethane and injected into HPLC system. In this analysis the TEA proved to be very valuable because of the presence of contamination. Winches-

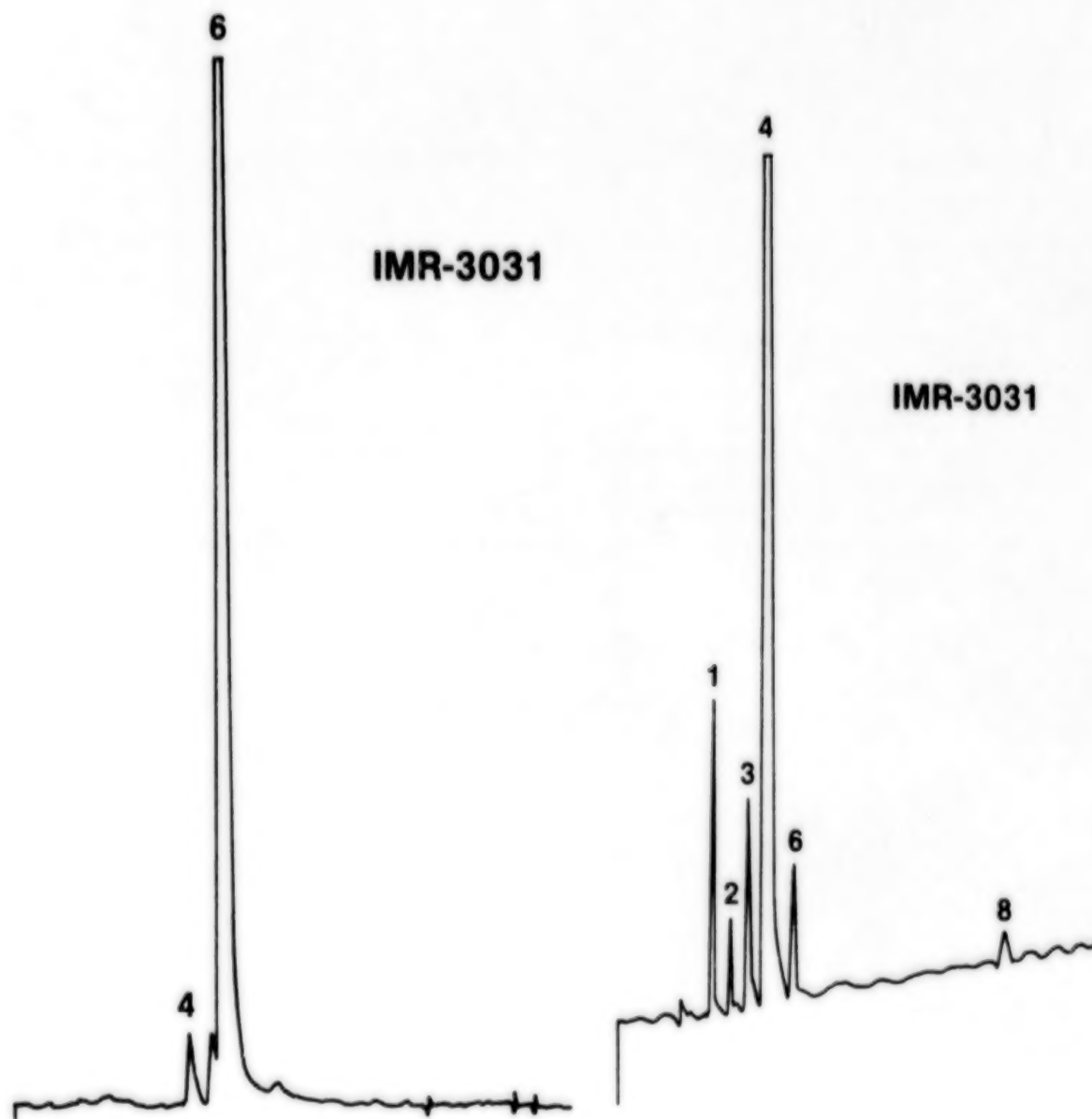


Figure 8. Dupont IMR-3031 UV and TEA response 1. DPA, 2. 2-nitro DPA, 3. 2,6 DNT, 4. 2,4 DNT, 6. N-nitroso DPA, 8. DBP

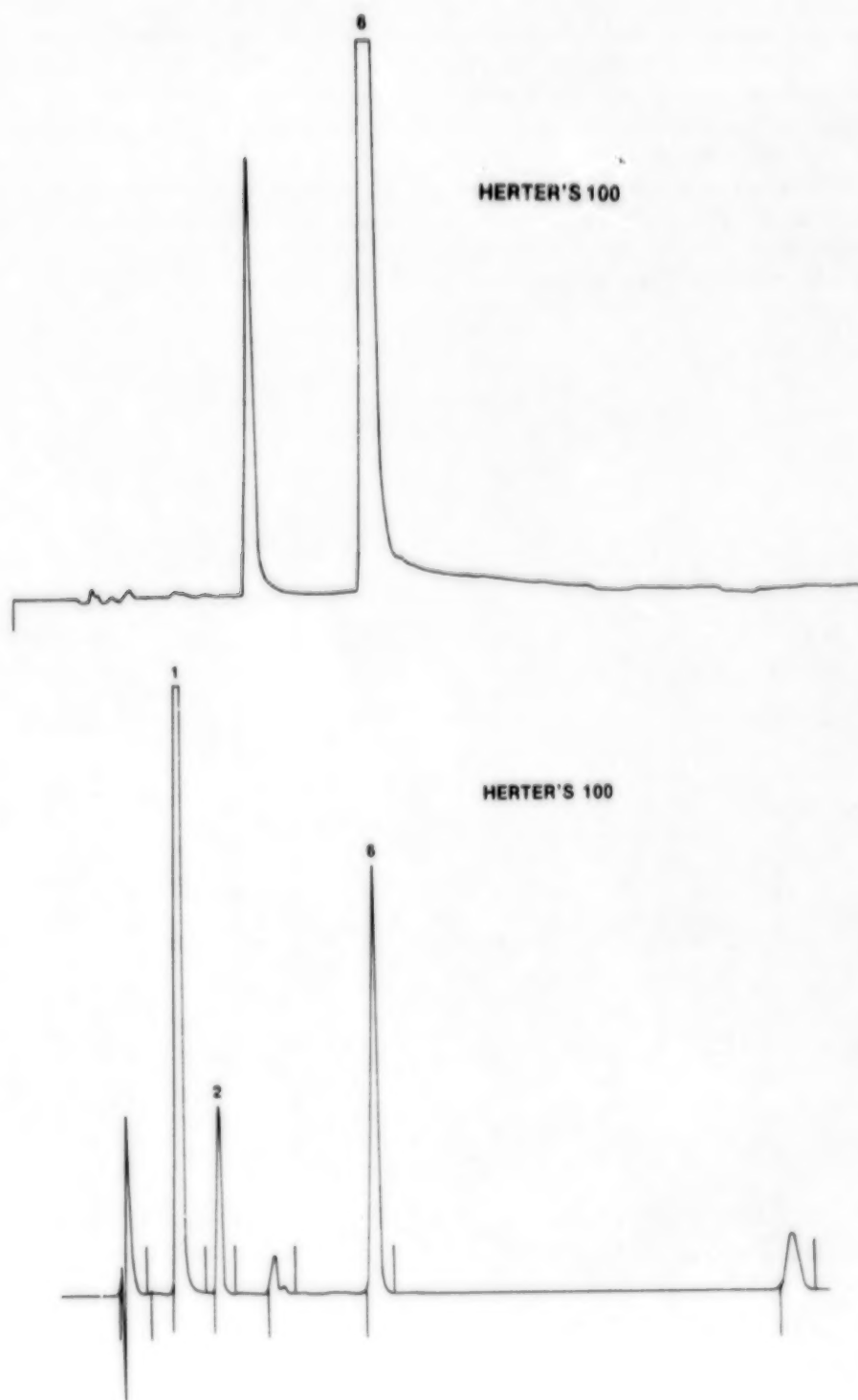


Figure 9. Herters 100 UV and TEA response 1. DPA, 2. 2-nitro DPA, 6. N-nitroso DPA

ter Western WW-760 was one of the powders used. On the UV chromatogram a large number of compounds were detected (Figure 11). (Probably originating from thread cutting oil) including 2,4DNT. None of the other common components in smokeless powder were found due to the contamination. The TEA was able to pick out NG and N-nitroso DPA which also implies DPA was present. From this information it could be concluded that the main charge was probably a ball powder. A single-base powder IMR-3031 was examined in

the same way. The only compound found was 2,4 DNT as would be expected. (Figure 12). The TEA showed no response for NG.

HPLC with UV/TEA detection proved to be a valuable technique for the analysis of smokeless propellants in forensic applications. Not only is it possible to determine the brand of powder and to do batch associations, but many inferences can be made in post blast situations where none of the powder remains.

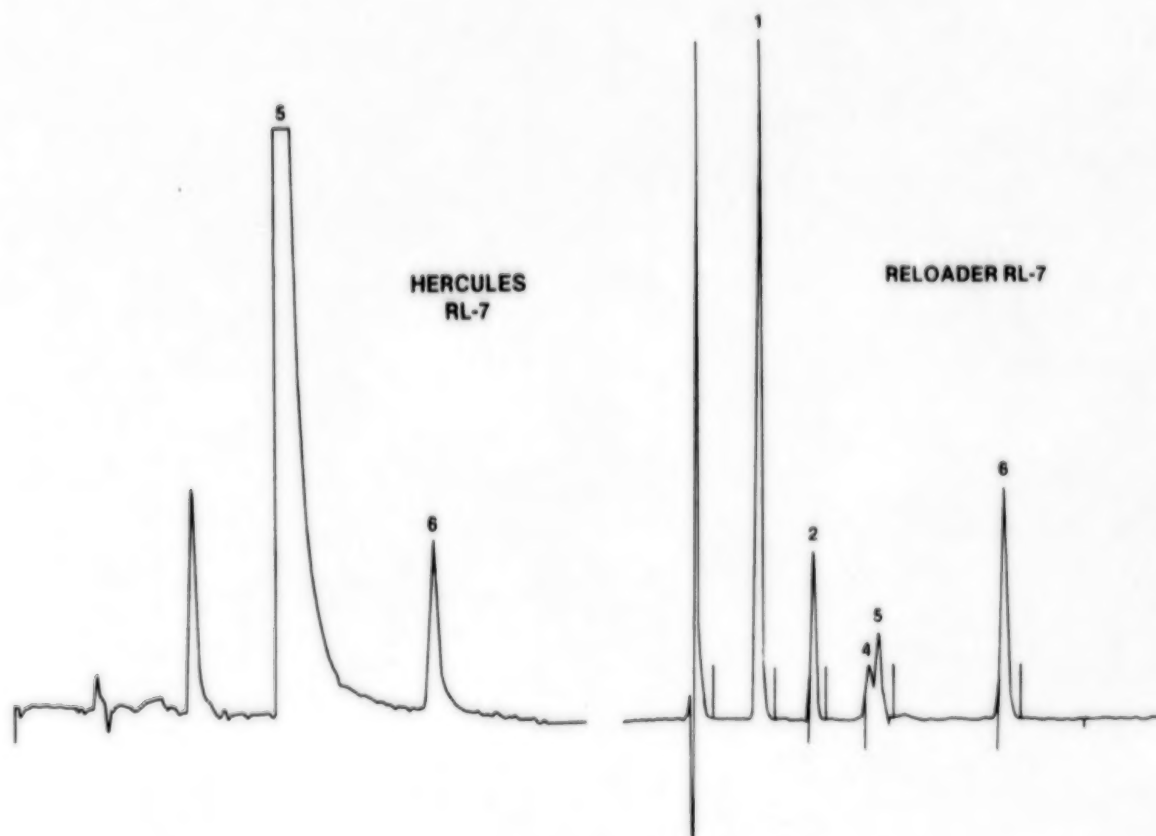


Figure 10. Hercules RL-7 UV and TEA response 1. DPA, 2. 2-nitro DPA, 4. 2,4 DNT, 5. NG, 6. N-nitroso DPA

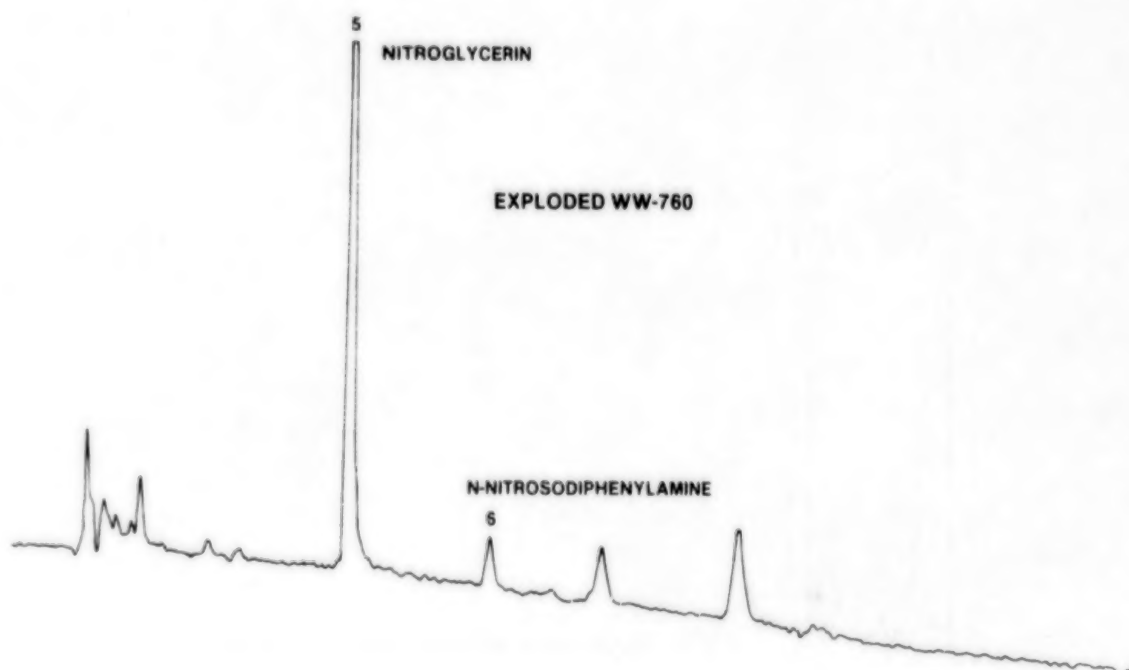
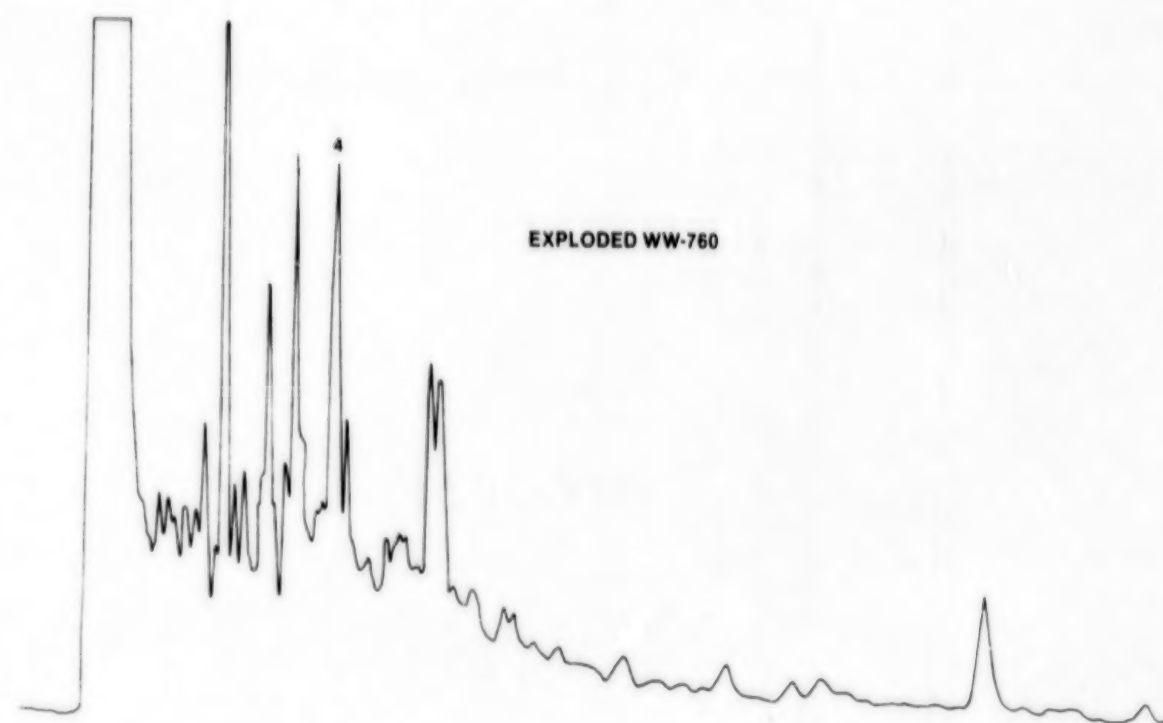


Figure 11. Exploded Winchester Western 760 UV and TEA response 4. 2,4 DNT, 5. NG, 6. N-nitroso DPA

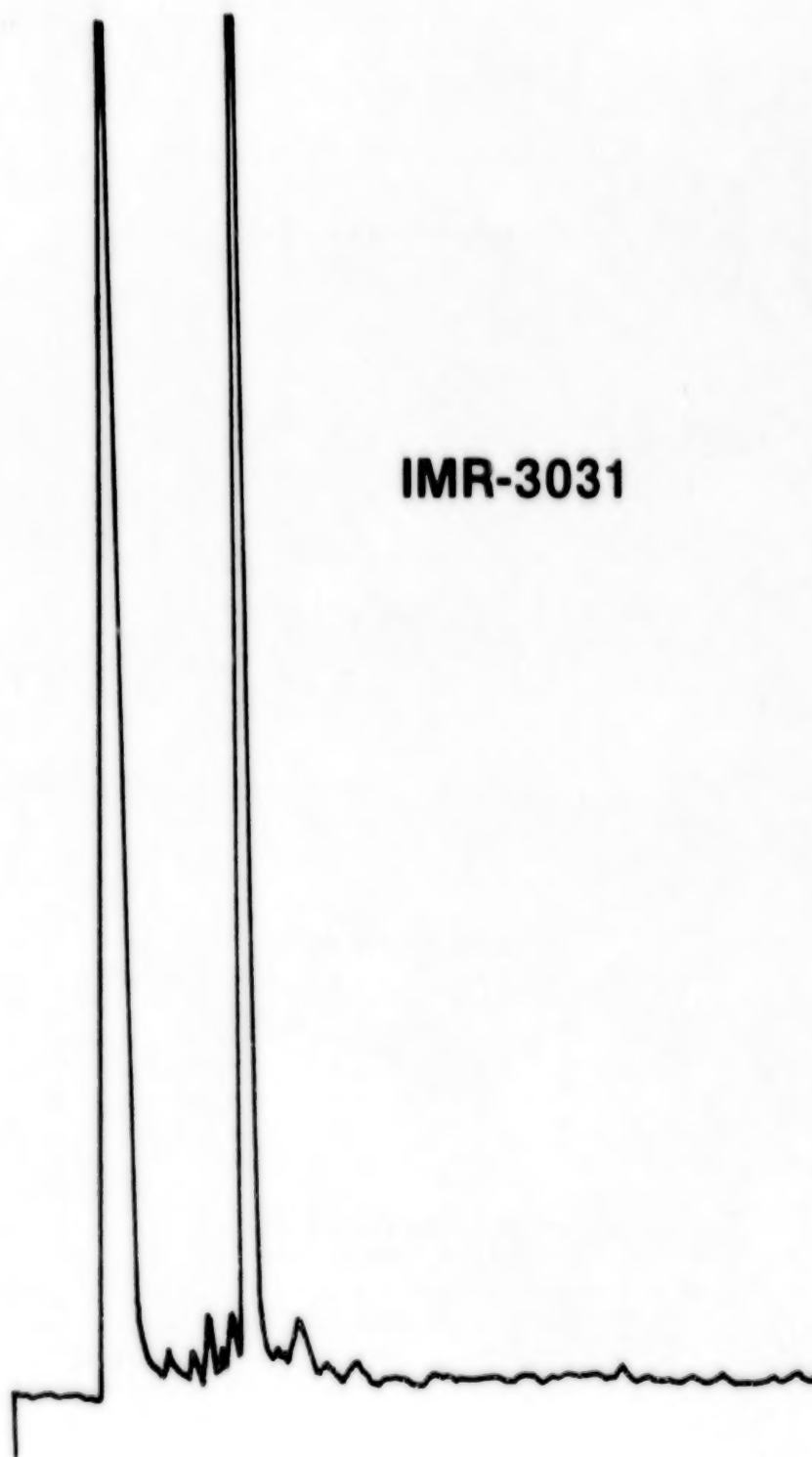


Figure 12. Exploded IMR-3031 UV response



## DETECTION OF EXPLOSIVE RESIDUES BY MICROBORE HPLC

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**ABSTRACT.** Microbore (1 mm I.D.) HPLC columns have aroused considerable interest of chromatographic workers. Considerable confusion exists over their reported claims of better sensitivity and better resolution. These points are clarified by specifying those chromatographic conditions which must be controlled for valid comparisons. Details for packing microbore columns are provided and their application to the analysis of traces of explosive residues is shown.

### INTRODUCTION

In the recent rise in popularity of 1mm I.D. packed LC columns (1,2,3), confusion has existed concerning their advantages over conventional bore (4–4.6 mm I.D.) packed LC columns. The reduced diameter of these microbore columns results in a clear-cut solvent savings (4). The very low flow rates (10–100  $\mu\text{l}/\text{min}$ ) mean easy interfacing of microbore HPLC systems and spectroscopic detectors such as MS, FTIR and NMR. There is, however, no reason to expect higher resolution or improved speed from microbore columns as these parameters are not governed by the column diameter, but, rather primarily by the diameter of the particles used to pack the column (5). Columns are routinely packed in our lab in longer lengths than those reported for conventional bore columns resulting in individual columns delivering very high resolution. However, conventional bore columns can simply be coupled producing the same high plate counts (6).

Microbore columns have the potential to deliver improvements in sensitivity, but only in cases where particular criteria are satisfied. "Column amplification" (7) results when the volume of solvent mobile phase containing a fixed amount of sample is reduced. This reduction in solvent volume is achieved by reducing the column diameter. The prerequisites needed in order to realize increased sensitivity are:

1. The same volume of sample must be applied to both conventional bore and microbore columns.
2. The same mass applied to both columns must be below the mass overload of both columns.
3. The geometry of the detector cell must be

identical in both cases.

We will now consider each of these points in detail.

1. The concomitant reduction in the volume of the peak with the reduction in column diameter means that unless a weak sample solvent is employed (8) (so that sample components in a large volume condense at the head of the column), the bandspreading caused by 10  $\mu\text{l}$  injection onto a microbore column will seriously reduce observed efficiency. However with weak sample solvent trapping, 25  $\mu\text{l}$  has been injected onto a microbore column in our lab with no loss in resolution. (9).

2. Column overload occurs when more than 0.1 mg of sample per gram of sorbent is injected on a column, and is characterized by skewed peaks. In most cases, compounds analyzed by LC have extinction coefficients high enough that sample charges do not exceed column overload concentrations. However, this is not always the case. The reduction in sample capacity parallels the reduction in solvent consumption in microbore columns. A typical microbore column has 1/20th the cross-sectional area of a 4.6 mm I.D. column. Thus, for equal column lengths and equal linear mobile phase velocities the microbore will use 1/20th the mobile phase volume, and accommodate only 1/20th the sample mass. A conventional bore and microbore column both operated at column capacity will deliver exactly the same sample concentrations to a detector cell resulting in identical sensitivities for both systems (assuming the same detector is employed). However, in cases where only a limited amount of sample is available (such as forensic applications and some areas of biomedical research) the microbore system will in-

deed deliver a higher concentration to the detector cell for a fixed sample mass provided this mass does not overload the column.

3. The reduced peak volumes from microbore columns may require a reduction in the detector cell volume in order to reduce extra column band broadening and maintain resolution. If the path length of the cell is reduced, so is the sensitivity. If sensitivity is the goal, some sacrifice in resolution must be made in order to maintain sensitivity. Peak width, expressed as the square root of the variance ( $\sigma$ ) is

$$\sigma = \frac{(1 + k')V_0}{\sqrt{N}}$$

where  $k'$  is the capacity factor,  $V_0$  is the void volume and  $N$  is the number of theoretical plates. It has been shown (9) that if the square root of the variance of the peak and the volume of the detector cell are equal, there will be less than a 5% increase in the observed peak width caused by the static volume of the cell at low flow rates. Given a well packed 10 micron, 50 cm microbore column producing 25,000 theoretical plates, conventional 8  $\mu$ l volume detector cells can be used as long as the  $k'$  exceeds 4, with less than a 5% reduction in resolution caused by this large cell volume. This means that, given a tight, low volume connection to the cell, many conventional detectors can be used with microbore columns. Depending upon the complexity and concentration of species present in a sample, detector cells can be chosen to provide either high resolution or high sensitivity.

This paper will demonstrate by the use of microbore columns in the analysis of trace levels of explosives on post-explosion debris.

### EXPERIMENTAL

A MACS (Micro-Analytical Chromatographic System, EM Science, Gibbstown, NJ) was used for all analyses. This includes the MACS Model 500 0.5  $\mu$ l internal loop injector connected by a 3.6 cm x 0.010" I.D. coupling to a microbore column. The MACS Model 700 variable wavelength UV detector was used with either the 0.5  $\mu$ l or 8.0  $\mu$ l detector cells (path lengths of 1 and 10 mm, respectively).

The column terminates directly at the detector cell. The volume between the column outlet and the optical path was less than 1  $\mu$ l in the 0.5  $\mu$ l cell, but the 8.0  $\mu$ l cell has a 4  $\mu$ l volume prior to the entrance of the light path. This was removed by inserting a 0.010" I.D. teflon capillary tube in this

volume, reducing it to  $\leq 1 \mu$ l. Chromatograms run before and after this procedure showed both an increase in sensitivity and resolution (1.5-2  $\times$ ) using the cell with the smaller inlet volume.

### COLUMNS

A 1 mm x 50 cm microbore column packed with LiChrosorb RP-18, 7  $\mu$  (E. Merck, Darmstadt, Germany) was prepared using slurry packing with 95/5  $\text{CCl}_4/\text{CH}_3\text{OH}$  (5 ml slurry solvent to 0.32 g sorbent) driven with MeOH at 10,000 psi. Tubing (1/16" O.D. x 1 mm I.D.) was manually polished on the inside using string and abrasive. This procedure is essential to obtaining good columns and deserves some comment.

Glass has been shown (10) to be the best surface for packed capillary (0.35 mm I.D.) LC columns and it is believed the smoothness of the glass is responsible for its high performance. Glass-lined microbore columns are available commercially (Whatman, Clifton, NJ). Homemade glass-lined stainless steel columns have several disadvantages over polished stainless steel columns, including:

1. Their 1/8" O.D. requires the use of bulky endfittings, making direct connection to the detector cells impossible. An additional outlet transfer tube must be used, which at low flow velocities does not degrade performance, but does add to the plate height at high flow rates.

2. They are inflexible, making connections to instrumentation more difficult than 1/16" microbore columns.

3. The high cost (\$25 as opposed to \$2 for 1/16" stainless steel tubing) of the column blank.

4. The imprecision in end fitting installation coupled with not knowing if the glass has been crushed when seating the ferrule.

Certainly good columns can be made with glass-lined stainless steel tubing. The polishing procedure on 1/16" stainless steel tubing makes use of glass-lined tubing unnecessary, avoiding the problems above.

### POLISHING PROCEDURE

The polishing procedure involves clamping the 1/16" column in place using two vices, protecting the tubing from crushing by surrounding it with thickwalled rubber tubing. A doubled strand of thin thread is pulled through the tube with a vacuum pump. A thicker thread (*i.e.* button and carpet thread) is pulled through as a loop, followed by this thicker loop pulling as much thread as can be comfortably pulled without breaking the

threads. White polishing compound (E. I. DuPont de Nemours and Co., Wilmington, DE), commonly used to remove oxidized paint from automobiles, is applied to the threads and polishing proceeds by pulling the coated strings back and forth for 5-10 minutes with the generation of considerable amount of heat. A clean thread bundle is inserted and the process is repeated, followed by a final bundle which is not coated with abrasive and is used to buff the inside of the tube and remove traces of polishing compound. Visual inspection of the interior of the tube reveals elimination of interior surface roughness. This roughness was the cause of the early failure of many commercial microbore columns (void formation, loss in efficiency) as well as their low original performance. Reduced plate heights of 2 are usually obtained using polished tubing.

## SAMPLES

TNT, RDX and PETN as well as simulated explosion residue samples were obtained through the FBI Academy, Quantico, VA. Explosion wreckage was generated by blowing up sections of a galvanized steel trash can, and since these tests took place outside, samples collected afterwards were encrusted with varying amounts of mud and rocks. Extraction was performed by spraying these irregular shapes with 25 ml of acetonitrile and collecting the run-off in 600 ml beakers. Aliquots were either directly injected or concentrated 10 $\times$  by blowing down with nitrogen prior to injection.

## RESULTS

Conditions for all analyses is shown in Table 1. Figure 1A shows explosive standards injected at

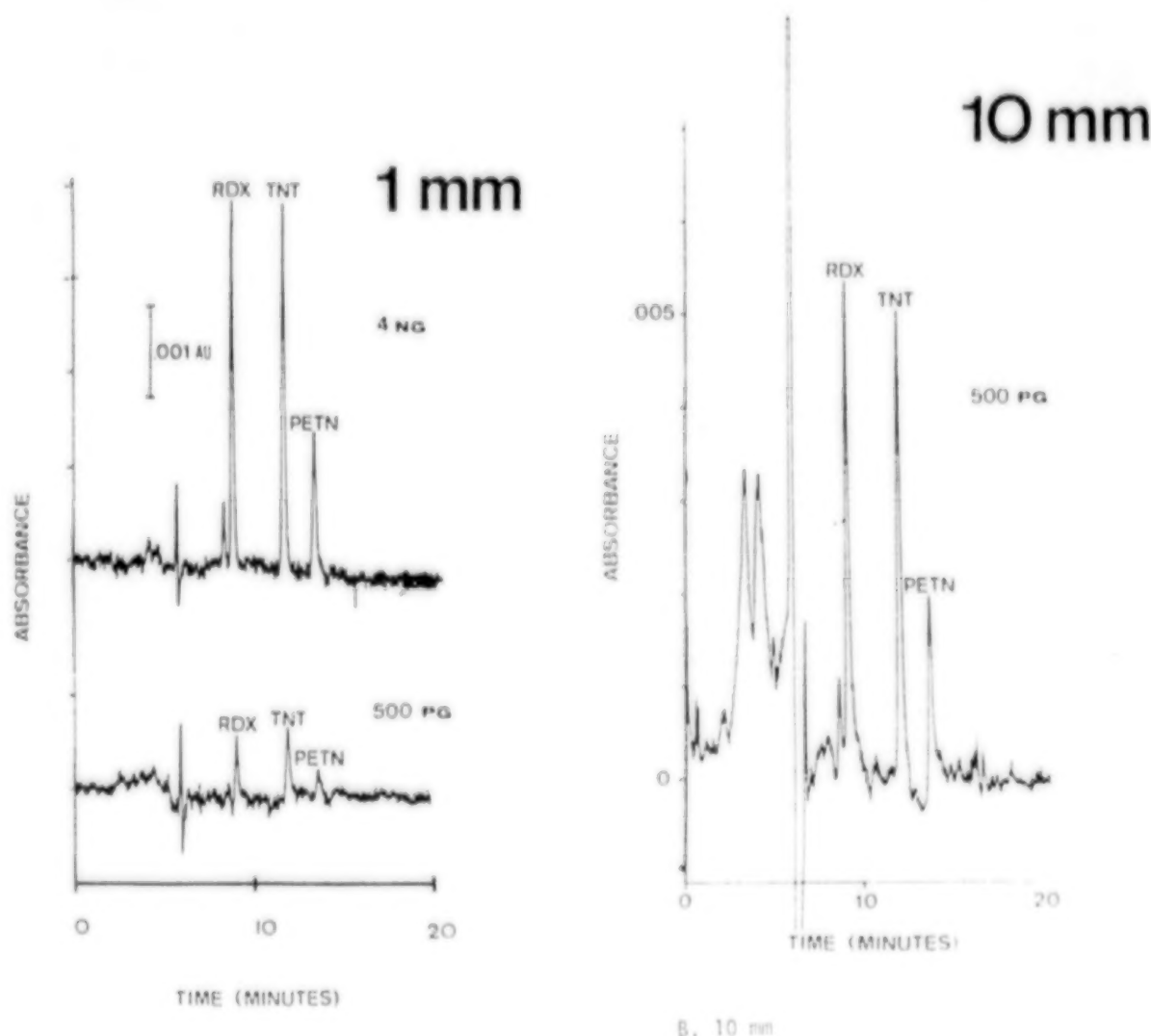


Figure 1. Sensitivity in Microbore HPLC for Detector Cells of Different Pathlengths.

TABLE 1

	Conditions
Column	50 cm $\times$ 1 mm ID
Sorbent	LiChrosorb RP-18, 7 $\mu$
Solvent	2:1 Acetonitrile: Water
Flow Rate	50 $\mu$ l/min
Pressure	800 PSI
Detector	UV @ 210 nm
Sensitivity	0.01 Absorbance Units
Time Constant	1 second
Temperature	Ambient (22°C)

levels of 8 ng/ml and 1 ng/ml, giving a detection limit of 100–500 pg in the 1 mm pathlength 0.5  $\mu$ l detector cell. By switching to the 10 mm pathlength 8.0  $\mu$ l cells (Figure 1B), peak heights are increased, but so is baseline noise. The longer pathlength provides greater sample sensitivity but is also more sensitive to small temperature fluctuations which causes refractive index changes resulting in increased noise. The frequency distribution of this baseline noise is typically lower than the frequency spectrum of eluting peaks. In principle,

it should be possible to filter out the low frequency noise but the procedure would require the use of complex digital filtering techniques as opposed to the simple analog low pass filter available on the MACS. It should also be possible to reduce the noise by carefully matching the temperature of the column and the cells, thus reducing changes in the refractive index of the solvent as it traverses the light path. In the present case, absolute peak height is improved 8 times going to the 8  $\mu$ l volume cells. Depending upon which definition of noise is used, the noise increased 2–3 times, resulting in an overall improvement in sensitivity of 3–4 times. Resolution was reduced, going from 32,000 plates with the 0.5  $\mu$ l cells down to 22,000 plates with the 8.0  $\mu$ l cells (measured on RDX, Peak #3).

Figures 2–4 demonstrate the sensitivity and resolution of microbore HPLC in the analysis of trace explosive residues.

Figure 2 shows that the concentration of PETN recovered from the post blast residue was twice the

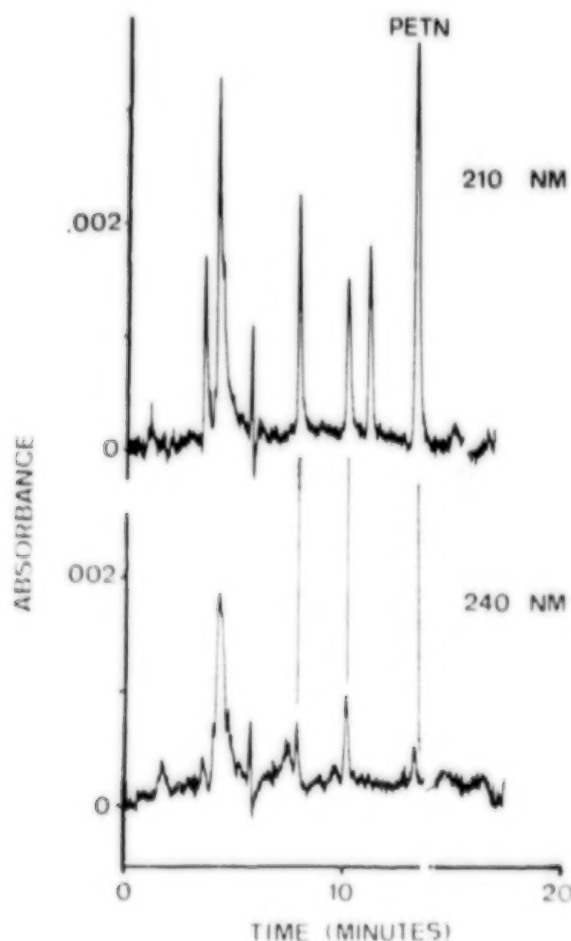


Figure 2. PETN Analysis at 210 and 240 nm.

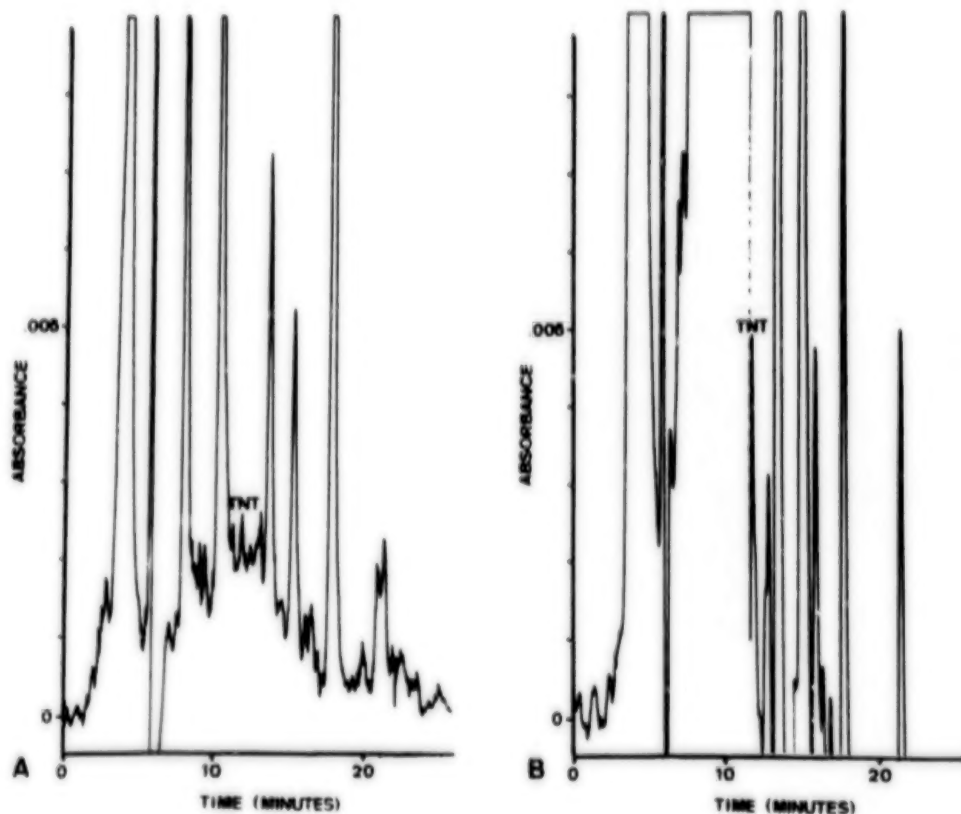


Figure 3. Analysis of TNT. A. Original Extract. B. 10X Concentration of Original Extract.

8 ng/ml standard, meaning the total amount available on the original sample was 200  $\mu$ g. The peak in the explosive residue sample which eluted at the same time as the PETN standard showed the correct absorption ratio at 210/240 nm, thus increasing the confidence that this peak was PETN.

Figure 3 showed a more complex matrix for the TNT sample. Nevertheless, the microbore column was able to distinguish TNT from over 100 other peaks in the sample (only a part of the chromatogram is shown). Ten-fold concentration of the initial extract resulted in the baseline being off-scale during the elution of the TNT peak, but auto-zeroing just prior to the TNT's elution (Figure 3B) did reveal a peak at the proper retention time with ten times more height.

Figure 4 shows the least definitive identification, that for RDX. It appeared as a shoulder on one peak, and, unfortunately, when run at other wavelengths the surrounding peaks obscured it. In this case, the use of more specific detectors (TEA (11), ECD (12), EC (13)) would have been needed for confirmation of this species.

## CONCLUSION

Microbore HPLC provides sufficient sensitivity and resolution for the detection of trace explosive residues in real samples. Its advantages over conventional bore columns is that it uses less solvent and in the case of limited samples can provide increased sensitivity.

## ACKNOWLEDGEMENTS

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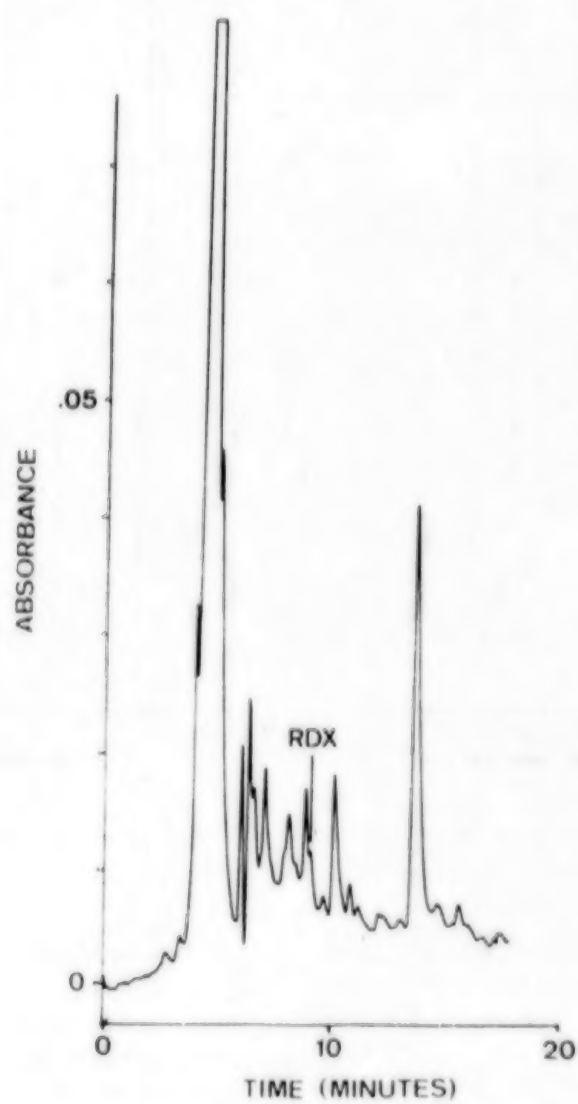


Figure 4. RDX Analysis



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# DETERMINATION OF NITRATE ESTERS, NITRAMINES, NITROAROMATICS, AND THEIR METABOLITES IN BIOLOGICAL FLUIDS AND WASTEWATER BY GAS AND LIQUID CHROMATOGRAPHY WITH A NITRO/NITROSO SPECIFIC DETECTOR

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**ABSTRACT.** As a consequence of work with cardiovasodilators, the capability now exists to evaluate the potential occupational hazard associated with human exposure to explosives via skin contact and/or vapor inhalation in biological fluids. A technique using the TEA<sup>®</sup> Analyzer interfaced to a gas chromatograph (GC) or a high-performance liquid chromatograph (HPLC) is described for the trace level determination of nitroglycerin, pentaerythritol tetranitrate, and their metabolites in blood. The method developed is capable of detecting 0.1 nanogram of each of the nitrate esters. The precision of the HPLC-TEA method at 1 ng/ml (ppb) level was established to be 7.4% and 5.7% relative standard deviation (RSD) for nitroglycerin and pentaerythritol tetranitrate, respectively. Analytical methodologies developed for the detection of cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), cyclotetramethylene tetranitramine (HMX) in biological matrix and wastewater effluents are also discussed.

## INTRODUCTION

The manufacture of explosives is an important industry related to national defense, commerce, industrial blasting and demolition. According to the 1976 estimates by the National Institute for Occupational Safety and Health (NIOSH), approximately 8000 workers in the U.S. dynamite industry are exposed to nitroglycerin (NG) either alone or in combination with ethylene glycol dinitrate (EGDN). During 1981, the Bureau of Mines estimated that 4.3 billion pounds of explosives were manufactured in the United States, 65% of which were consumed in the coal mining industry. In the pharmaceutical industry, nitrate esters such as nitroglycerin, pentaerythritol tetranitrate (PETN) and isosorbide dinitrate (ISDN) are frequently used as coronary vasodilators for the therapeutic treatment of angina pectoris and acute

myocardial infarction. Nitroglycerin oral tablets, for example, have been prescribed for the fast relief of acute anginal pain because of its rapid onset effect on the dilatation of blood vessels.

Occupational exposure can either be through vapor inhalation or skin absorption, or a combination of both (Bishop *et al.* 1981; Gotell, 1976; Hogstedt and Stahl, 1980; Hogstedt and Davidson, 1980). For an eight hour time-weighted average exposure of about 1 mg/m<sup>3</sup> EGDN in the air, it is estimated that a blood level of a maximum 2 ng/mL EGDN would be observed (Gotell, 1976). However, the major route of exposure is through skin contact, accounting for over ninety percent. Historically, the typical symptoms of exposure to explosives are headaches, dizziness, nausea, heart palpitations and in severe cases, death may occur (Carmichael and Lieben, 1963; Lund *et al.* 1968;

Morikawa *et al.* 1967). In the environmental area, effluents from the operation of munitions manufacturing could lead to the contamination of sea, ground and surface water, soils and sediments, all of which may pose a potential health hazard. Trinitrotoluene (TNT) has been identified in the ground water after leaching from disposal sites (Pereira *et al.* 1979). Over thirty (30) nitroaromatic compounds were identified in the wastewater effluent generated in the manufacture of TNT (Spanggord *et al.* 1982). NG and degradation products were determined in wastewaters (Chandler *et al.* 1974), and EGDN was identified in drinking water (Fan *et al.* 1978).

The toxicity and toxic effects of TNT are well-documented (Crawford, 1954; Djerassi and Vitany, 1975; McConnell and Flinn, 1946; Morton *et al.* 1976) and its occupational exposure has been reported to occur by inhalation, skin absorption, and injection. Tetryl, a nitroaromatic explosive, has been tested to be mutagenic in three microbial test systems (Whong *et al.* 1980). The toxic effects of RDX in humans has been associated with epileptiform seizures (Barsotti and Crotti, 1949; Kaplan *et al.* 1965).

In light of worker exposure and the potential health hazard associated with it, NIOSH in 1976 proposed a ceiling concentration of 0.1 mg/m<sup>3</sup> for NG and EGDN for a 20 minute sampling period. The U.S. Department of the Navy's Bureau of Medicine and Surgery (BUMED) has identified five constituents of ordnance-disposal waste—ammonium picrate, picramic acid, propylene glycol dinitrate, RDX, and TNT—as potential contaminants of drinking water, and has established a target interim maximal contaminant level for drinking water. (National Academy Press, 1982).

To assess the occupational exposure of these compounds in environmental and biological matrices, it is necessary to develop viable analytical methodologies and sensitive instrumentation. The TEA analyzer has been demonstrated to be a sensitive and selective detector for nitro-based compounds (Goff *et al.* 1983); LaFleur and Morriseau 1980; Yu and Goff, 1983). Its application for the explosives in post-blast debris, post-blast air sample, and handswabs was already presented in an earlier report (Fine *et al.* 1983). In this paper, we describe its application in the environmental and biological areas.

## EXPERIMENTAL PROCEDURE

### Reagents

All solvents were distilled-in-glass grade (Burdick and Jackson). Glyceryl 1,2-dinitrate and 1,3-dinitrate (1,2-GDN and 1,3-GDN), glyceryl 2-mononitrate (2-GMN) and glyceryl 1-mononitrate (1-GMN) were synthesized by the method of Dunstan *et al.* (1965). Isosorbide 2-mononitrate and 5-mononitrate (2-ISMN and 5-ISMN) were obtained from Dr. John Markis, Beth Israel Hospital, MA. Sep-PAK C<sub>18</sub> cartridges (Waters Associates) and Miller-SR filters (Millipore Corporation) were used for sample preparation.

### Equipment

The liquid chromatograph (HPLC) was constructed with an Altex Model 110 solvent delivery pump (Altex Scientific Inc.) and a U6K universal injector (Waters Associates). A 10  $\mu$ m, 3.9 mm i.d.  $\times$  30 cm uBondapak CN column (Waters Associates) was used for the separation of isosorbide dinitrate, glyceryl trinitrate, and pentaerythritol tetranitrate, with a mobile phase consisting of iso-octane-methylene chloride-methanol (75:20:5) and at a flow rate of 1.5 ml/min. For the separation of the vasodilators and their respective metabolites a 10  $\mu$ m 4.6 mm i.d.  $\times$  25 cm Ultrasil NH<sub>2</sub> column (Altex Scientific Inc.) was used, with a mobile phase consisting of iso-octane-methylene chloride-methanol (80:13:7) at a flow rate of 2 ml/min. For the analysis of RDX and HMX, the cyano column was used, with a mobile phase consisting of isooctane-methylene chloride-methanol (60:30:10) at a flow rate of 1.5 ml/min. The amount injected onto HPLC was 10  $\mu$ L.

The detector was a TEA Model 510 analyzer (Thermo Electron Corporation) operating in the LC mode. The catalytic pyrolyzer temperature was maintained at 550°C. The carrier gas was nitrogen at a flow rate of 20 ml/min. Oxygen was maintained at a flow rate of 5 ml/min. The reaction chamber vacuum was 1.8 mm Hg. The cryogenic traps were maintained at -78°C with an ethanol-solid carbon dioxide slush bath.

The conditions for gas chromatograph—Thermal Energy Analyzer (GC-TEA) operation has already been discussed by Fine *et al.* (1983) in an earlier report of this symposium.

### Sample Preparation

#### A. Nitrate esters in plasma

Five ml of fresh frozen plasma (sampled immediately after thawing) were pipetted into culture

tubes and fortified with glyceryl trinitrate, isosorbide dinitrate, pentaerythritol tetranitrate, and selected lower nitrates at various levels. The samples were extracted with ethyl acetate (8 ml) and centrifuged to separate the two phases. The supernatant was transferred to a clean culture tube, and the plasma was re-extracted with  $2 \times 8$  ml ethyl acetate. The pooled extract was loaded onto a Sep-Pak  $C_{18}$  cartridge and clarified by a 0.5 micron Millex-SR filter. After concentration under a gentle stream of nitrogen at  $35^\circ\text{C}$  to 0.5 milliliter, the filtrate was transferred to a 1 ml vial and further concentrated to approximately two hundred microliters. Aliquots of the concentrated extract were injected on HPLC-TEA.

#### B. RDX in plasma

Five ml of plasma was fortified with RDX at the 5 ppb level, extracted with 16 ml of methylene chloride and pentane (1:1), clarified by filtration through a SEP-PAK  $C_{18}$  cartridge and a Millex-SR filter, concentrated under  $N_2$  to 0.2 ml, and analyzed by injecting 25  $\mu\text{l}$  onto HPLC-TEA.

#### C. Wastewater effluent samples

Ten ml of sample was loaded onto a preptube Type 117 (Thermo Electron Corporation) which was prewet with ten ml dichloromethane (DCM). The sample was eluted with  $8 \times 10$  ml DCM into a Kuderna-Danish evaporator. The eluant was evaporated at  $54^\circ\text{C}$  to 2 ml. Aliquot of the concentrated extract was injected onto HPLC-TEA and GC-TEA.

## RESULTS AND DISCUSSION

### Chromatography

The separation of the nitrate esters was achieved on a uBondapak CN column using isocratic conditions, as shown in Figure 1. The compounds were 1-ISDN, 11 ng; 2-NG, 5ng; and 3-PETN, 11 ng. When the column functionality was changed to the amino bonded phase, the lower nitrate metabolites of NG, ISDN, and PETN were resolved, as shown in Figures 2 and 3.

### Human Plasma Samples

The half-lives of the nitrate esters in the human blood stream are relatively short (Armstrong *et al.* 1979). They are rapidly degraded to the lower nitrate metabolites (Davidson *et al.* 1971; DiCarlo *et al.* 1968) which are more stable. To assess the occupational exposure, it would then be prudent to monitor the parent compounds, as well as the nitrated metabolites. Table 1 shows the recovery of

the nitrate esters and selected nitrated metabolites from human plasma at fortification levels ranging from 1 ng/ml to 80 ng/ml. Procedures for the analysis of the nitro-based vasodilators, at the blood level of 0.1–0.2 ng/ml, are now routine (Maddock *et al.* 1983; Spangord and Keck, 1980; Yu and Goff, 1983).

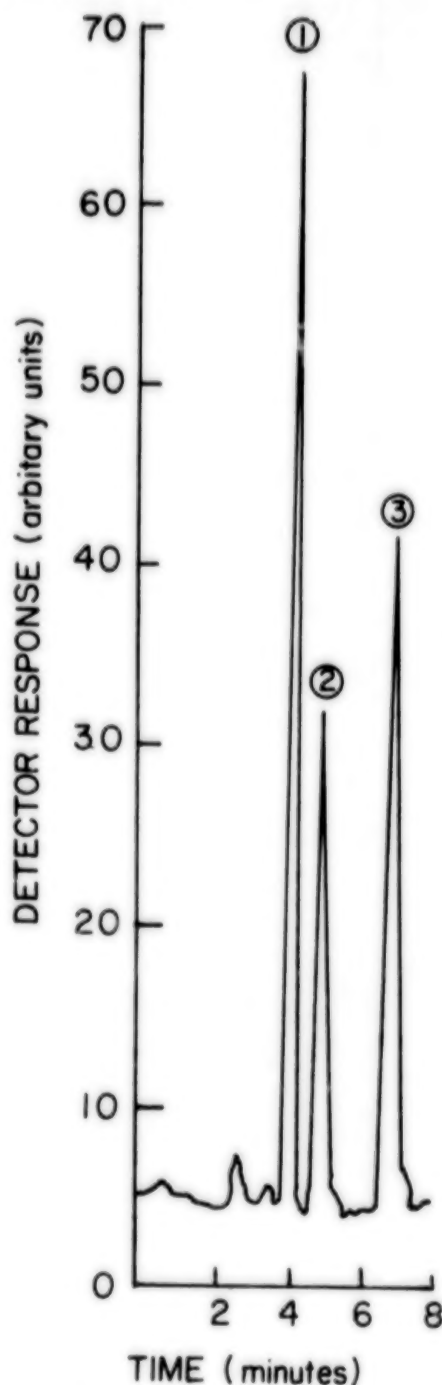


Figure 1. HPLC-TEA Chromatogram of Nitrate Esters: (1) isosorbide dinitrate, 11 ng (2) glyceryl trinitrate, 5 ng (3) pentaerythritol tetranitrate, 11 ng.

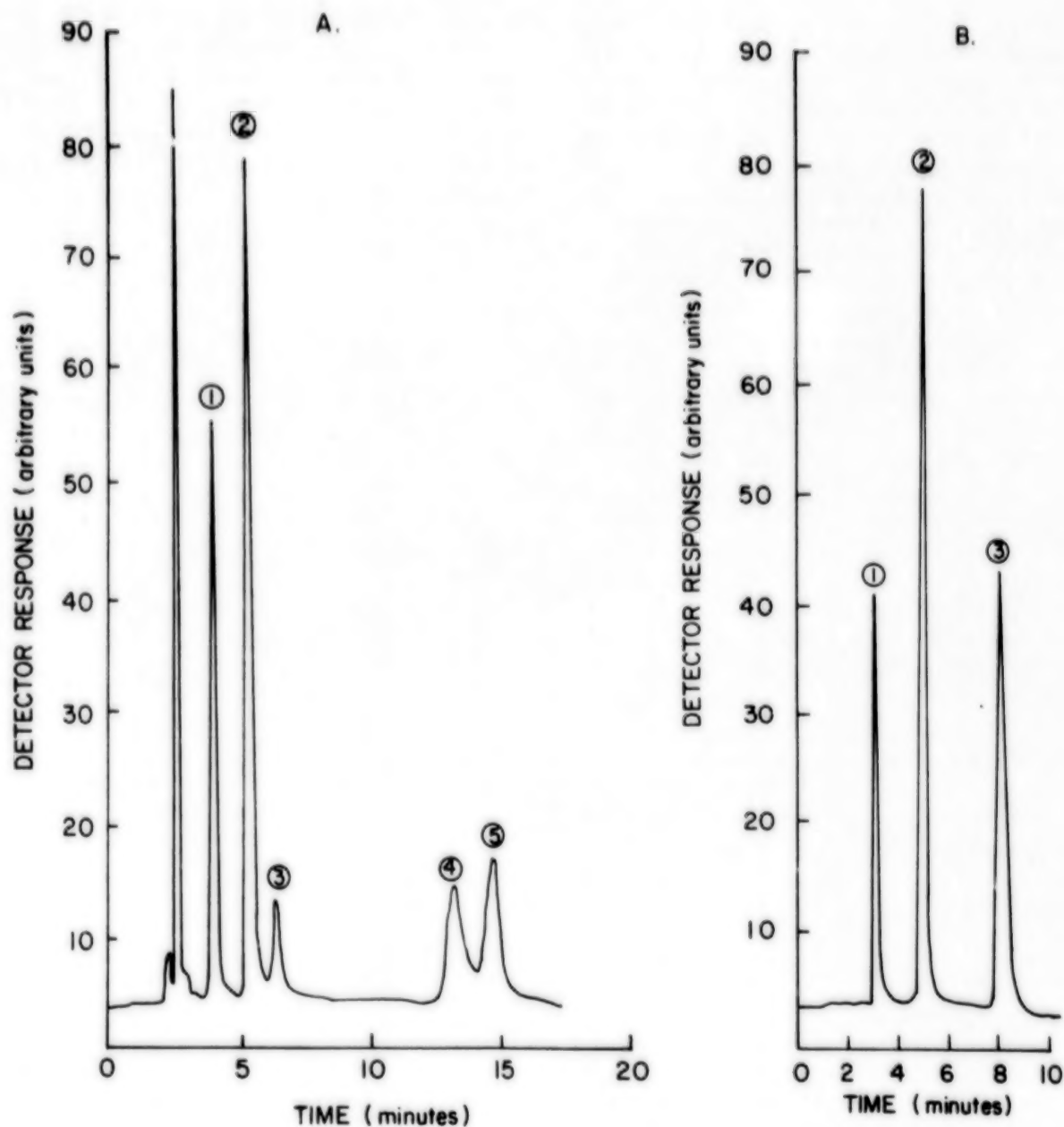


Figure 2. A. HPLC-TEA Chromatogram of Glyceryl Trinitrate and Metabolites: (1) glyceryl trinitrate, 2.5 ng (2) glyceryl 1,3-dinitrate, 3.7 ng (3) glyceryl 1,2-dinitrate, 0.7 ng (4) glyceryl 2-mononitrate, 2.2 ng (5) glyceryl 1-mononitrate, 4.4 ng B. HPLC-TEA Chromatogram of Isosorbide Dinitrate and Metabolites: (1) isosorbide dinitrate, 4 ng (2) isosorbide 2-mononitrate, 10 ng (3) isosorbide 5-mononitrate, 10 ng.



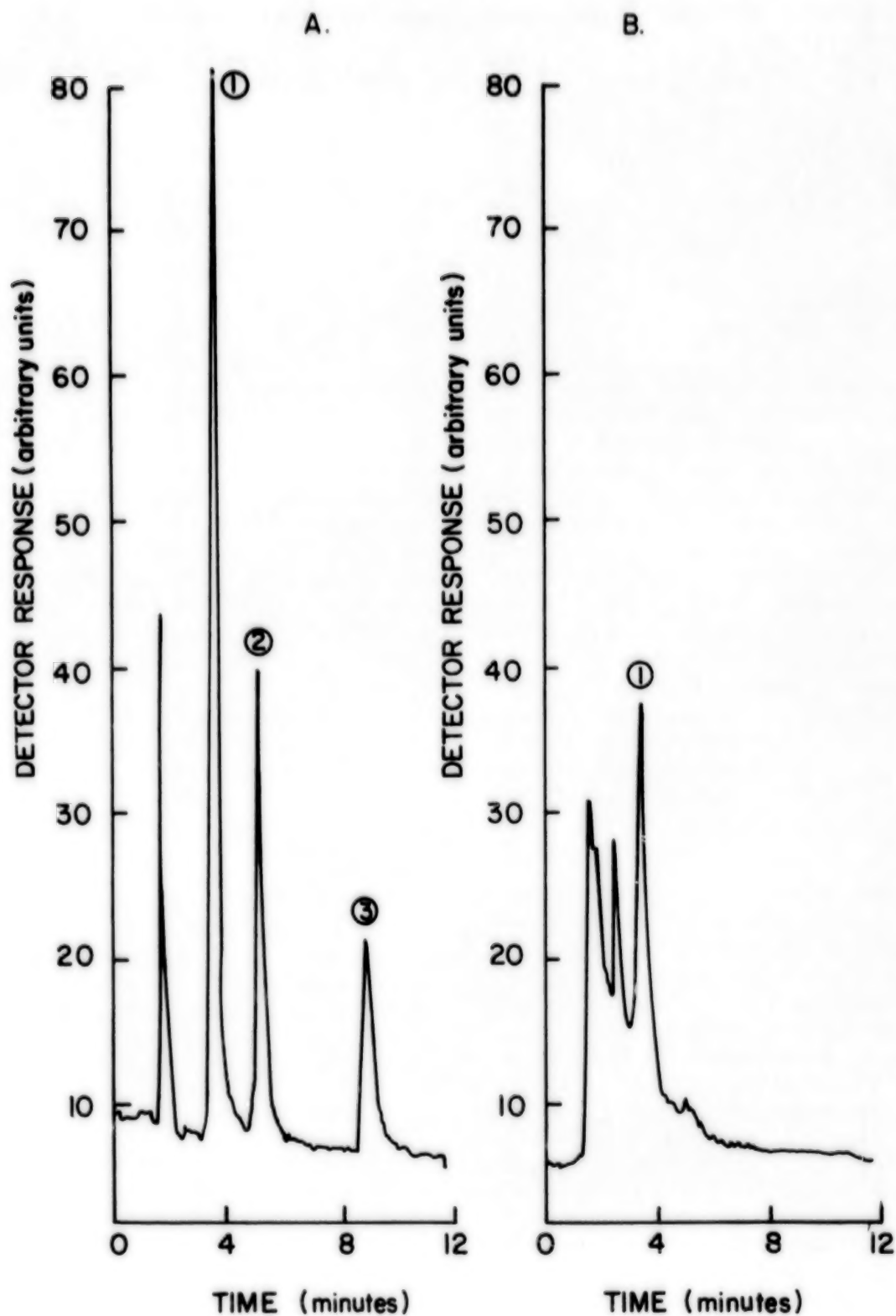


Figure 3. HPLC-TEA Analysis of Pentaerythritol Tetranitrate: A. Reference Standards (1) pentaerythritol tetranitrate, 5 ng (2) pentaerythritol trinitrate, 4.6 ng (3) pentaerythritol dinitrate, 13.6 ng B. plasma fortified with PETN at 10 ng/ml level.

**Table 1. RECOVERY OF NITRATE ESTERS AND NITRATED METABOLITES FROM PLASMA MEAN RECOVERY**  
(%,  $\pm$  S.D., n = 4)

ng/ml added	NG	ISDN	PETN	1,2 GDN*	1-GMN*	PETRIN*	PEDN*	2-ISMN*
1	54 $\pm$ 4	76 $\pm$ 6	67 $\pm$ 4	—	—	—	—	—
5	65 $\pm$ 7	62 $\pm$ 4	63 $\pm$ 4	91 $\pm$ 5	91 $\pm$ 15	61 $\pm$ 4	63 $\pm$ 4	85 $\pm$ 6
10	77 $\pm$ 6	80 $\pm$ 5	67 $\pm$ 2	—	—	—	—	—
20	74 $\pm$ 7	69 $\pm$ 5	71 $\pm$ 1	86 $\pm$ 3	60 $\pm$ 13	66 $\pm$ 4	60 $\pm$ 2	92 $\pm$ 12
40	82 $\pm$ 9	80 $\pm$ 5	63 $\pm$ 4	—	—	—	—	—
80	81 $\pm$ 5	65 $\pm$ 5	72 $\pm$ 4	—	—	—	—	—

\* Recoveries on these compounds were conducted at 5 ng/ml and 20 ng/ml only.

PETRIN—Pentaerythritol trinitrate

PEDN—Pentaerythritol dinitrate

In the experiments recently conducted by Twi-bell *et al.* (1982), NG could still be detected in a person's hands more than 20 hours after he had handled commercial explosives, even though his hands had been washed several times. Because of possible occupational hazards, there is a need to detect military explosives in human blood. This capability was explored with PETN and RDX. The chromatogram, shown in Figure 3, represents a plasma sample fortified with PETN at the 10 ng/ml level, and in Figure 4 for a 5 ng/ml RDX plasma spike. Because of the specificity of the TEA analyzer, interferences normally encountered in other detectors due to components such as proteins, glucuronides, and lipids present in plasma or blood do not represent a problem with the method.

#### Wastewater Effluents

Figure 5 shows the HPLC-TEA chromatogram of a wastewater effluent sample obtained from a munition manufacturing facility. HMX is identified in the sample, corresponding to 85 ng for a 5  $\mu$ l injection. The capability of the TEA analyzer interfaced to a gas chromatograph for another wastewater effluent analysis is demonstrated in Figure 6. In this sample, 2,4-DNT, TNT, and RDX were present (retention times 7.33, 8.76, and 10.03 minutes, respectively). In addition, two other TEA peaks were observed at the retention time of 1.78 and 3.39 minutes. Given the matrix complexity of wastewater effluent where a number of other nitro-containing compounds may be present, the TEA technique could be used to selectively screen for all nitro compounds.

A comparison study of the TEA analyzer with three other GC detectors: electrolytic conductivity (HECD), thermionic (TSD) and electron capture (ECD), has been made for the analysis of nitroaromatics such as nitrobenzene, and isomers

of dinitrotoluenes in sludge wastes by Phillips *et al.* (1983). The analysis of trace components in industrial or municipal sludge is extremely difficult owing to matrix complexity. Figure 7 shows the chromatograms of the spiked sludge extract obtained using the ECD, HECD, TSD and TEA. The shaded areas correspond to the response of each detector for the spiked nitroaromatics—nitrobenzene, 2,4-DNT, and 2,6-DNT—in the sludge extract produced by superimposing the standard response onto the individual chromatograms.

In the chromatograms obtained using the first three detectors, it was observed that a multitude of interfering peaks co-elute or elute at retention times close to the nitroaromatics, making accurate quantitation difficult. For the TEA, besides a broad "solvent peak", the only peaks observed were due to nitrobenzene, 2,4-DNT, and 2,6-DNT. While all four detectors have inherent sensitivity towards standard nitro compounds, only the TEA analyzer can selectively detect the nitro compounds in the sludge samples. The use of the TEA analyzer does preclude the necessity for any further sample clean-up.

#### CONCLUSION

Analytical methods are developed for the trace analysis of various explosives and their nitrated metabolites in human plasma and wastewater effluent. Monitoring and assessment of worker exposures to these compounds can now be routinely conducted through the use of the TEA analyzer.

#### ACKNOWLEDGEMENT

We thank Air Products for permission to reproduce their chromatograms, shown in Figure 7.

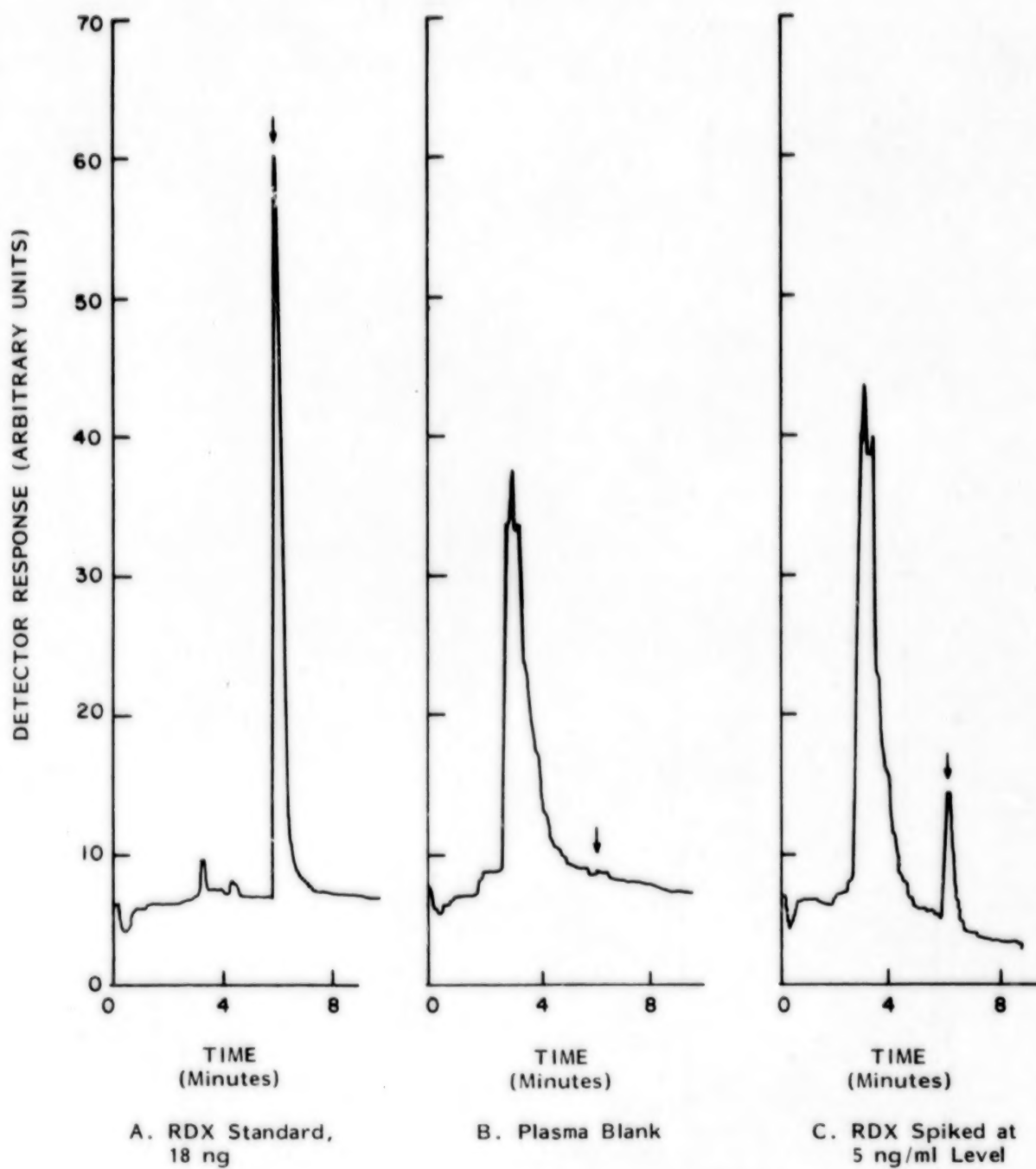


Figure 4. HPLC-TEA Analysis of RDX in Plasma.

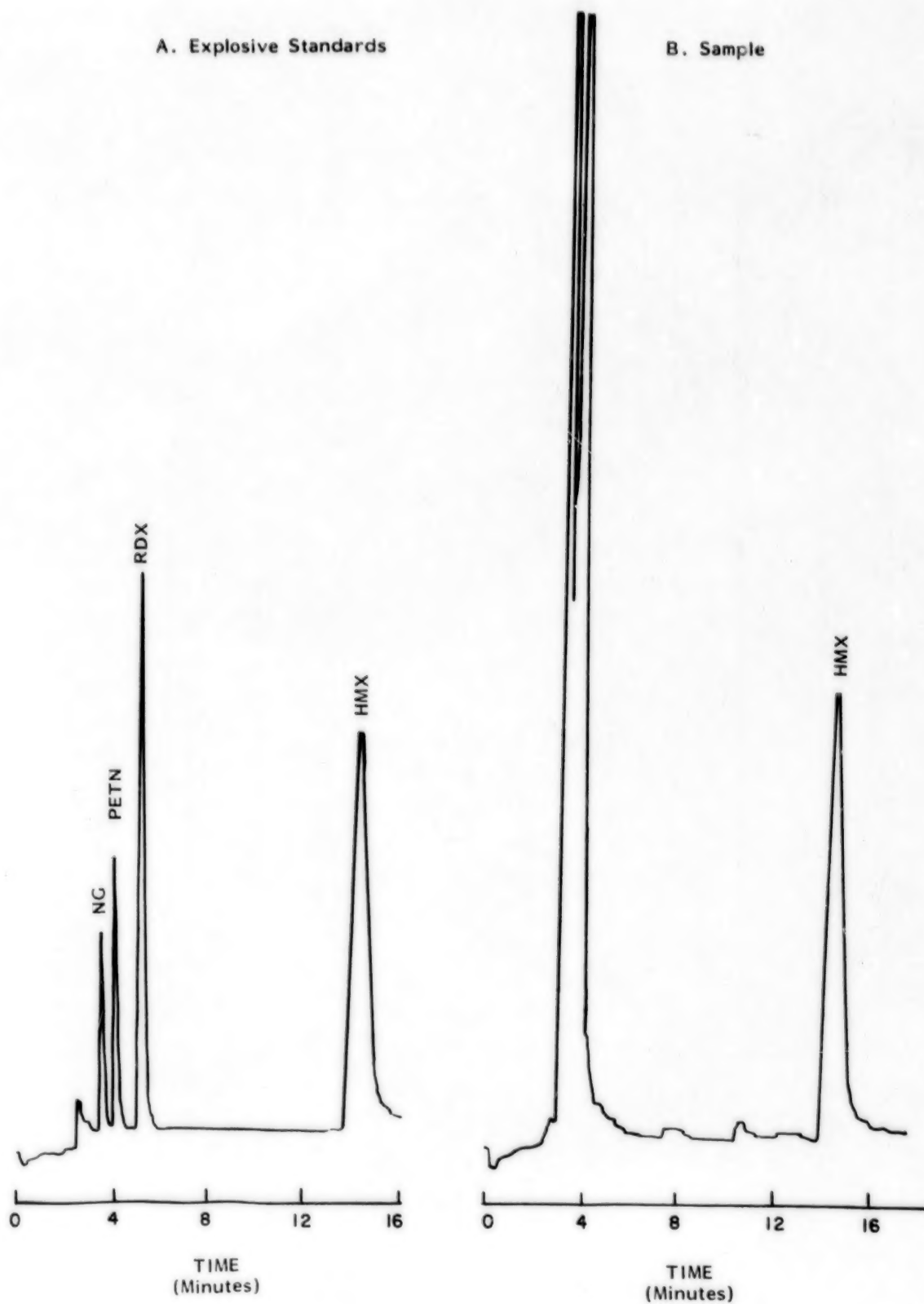


Figure 5. HPLC-TEA Analysis of Wastewater Effluent A. Standard explosives B. Sample analysis.

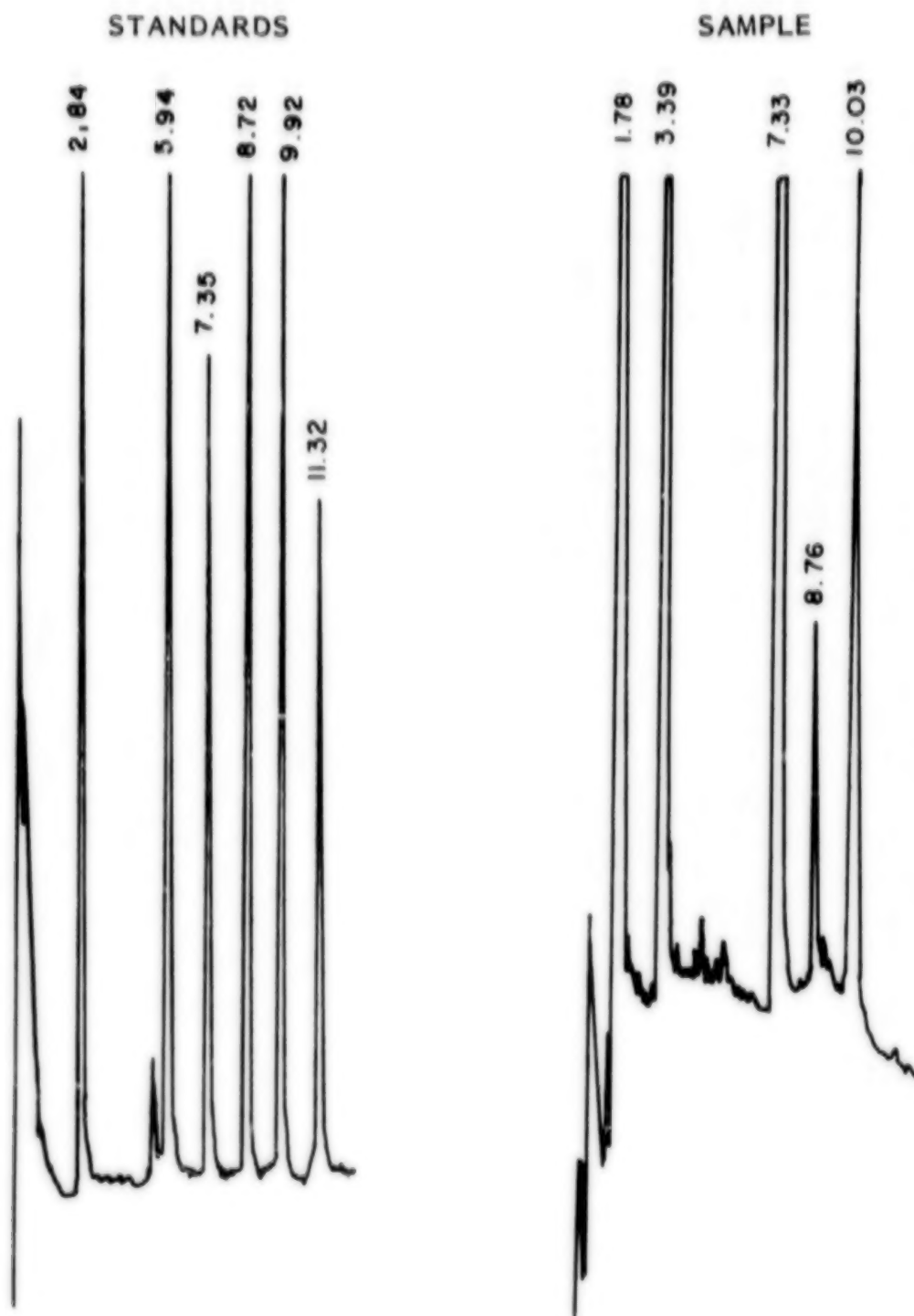
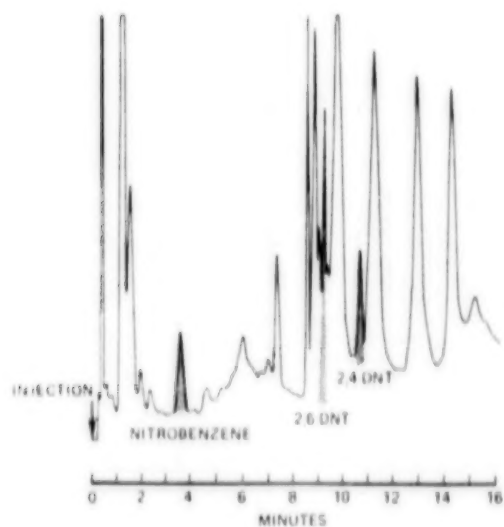
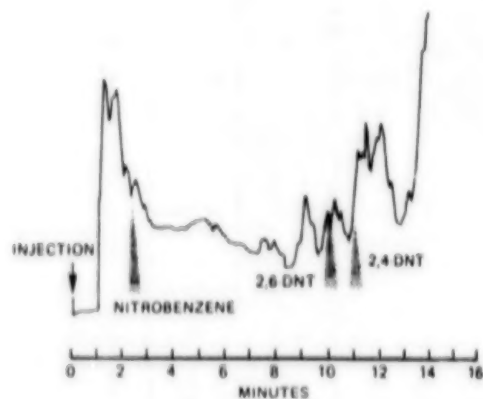


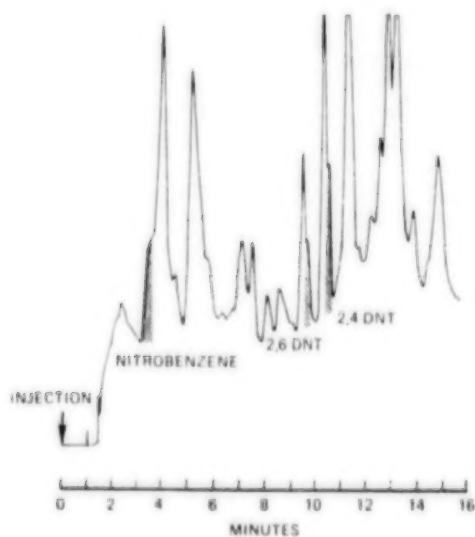
Figure 6. Capillary GC-TEA Analysis of Wastewater Effluent Standards—EGDN (2.84 min.), NG (5.94 min.), 2,4-DNT (7.35 min.), TNT (8.72 min.), RDX (9.92 min.), Tetryl (11.32 min.).



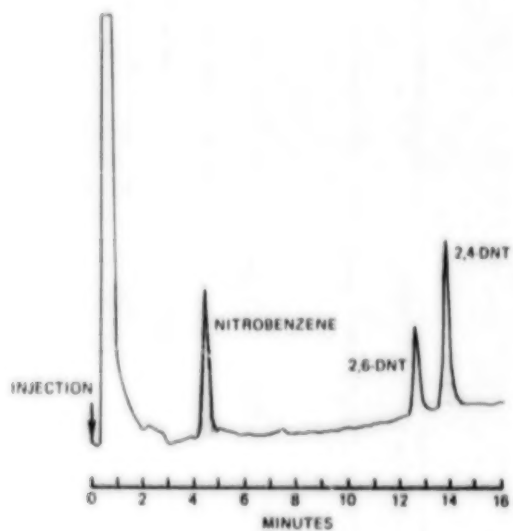
ELECTRON CAPTURE



HALL ELECTROLYTIC



THERMIONIC



TEA

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Figure 7. Comparison of Four Selective GC Detector for Nitroaromatics.



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## EXPLOSIVES AND GUNSHOT RESIDUE DETECTION BY APPLICATIONS OF ELECTROCHEMISTRY

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**ABSTRACT.** Reductive and oxidative electrochemical detection with liquid chromatography is applied to the determination of nitro aromatics, nitrate esters, nitramines, and diphenylamines in military explosives and double base smokeless gunpowders. A sensitive and highly selective method is presented for the detection of organic "gunshot residue" on the hand of individuals who have discharged a weapon. The detection limits are of the order of 0.5, 1, 2, and 0.3 picomol for nitro aromatic, nitramine and nitrate ester explosive compounds, and diphenylamines, respectively. In the last five years, oxidative mode electrochemical detection in liquid chromatography has become widely accepted for solving many problems of clinical, pharmaceutical, and environmental interest. Several reviews have been published on the advantages resulting from the combination of liquid chromatography with electrochemical detection (l.c.-e.c.). Progress in reductive mode (l.c.-e.c.) has been slow because of problems associated with dissolved oxygen, metal impurities, and the lack of reliable electrodes. Recent technological advances in detector design and the availability of more suitable electrode materials has generated a renewed interest in this technique. This paper describes the application of reductive mode (l.c.-e.c.) using glassy carbon and amalgamated gold electrodes to quantify explosive compounds in military explosives and smokeless gunpowders, and the development of a highly sensitive and selective method for the detection of nitroglycerin, 2,4-dinitrotoluene (2,4-DNT), and diphenylamine (DPA) in gunshot residue. Most explosives can be classified into one of several groups represented by nitro compounds, nitro acid esters, nitramines, salts of perchloric and chloric acids, azides and other miscellaneous compounds capable of producing an explosion, and mixtures of explosives from the above groups. Representatives of common commercial and military explosive compounds suitable for trace determinations using reductive mode l.c.-e.c. will be discussed.

With the recent upsurge of terrorist and criminal activity and the widespread use of firearms, law enforcement officials and forensic chemists have been interested in finding an effective and inexpensive method to determine whether an individual has recently fired a weapon. This information is valuable in investigations of alleged suicides, armed assaults, homicides and other activities involving illegal use of firearms. In the

process of criminal investigations it is also necessary to ascertain whether an individual has fired a weapon or handled a weapon which has been recently fired.

As early as the 1930's, law enforcement officials observed the presence of nitrates on the hands of individuals after they fired a weapon. The "paraffin cast" or "dermal nitrate" technique was developed to measure residual nitrates. A paraffin

cast was formed on the suspect's hands and after peeling it off, the inside of the cast was sprayed with diphenylamine reagent solution. The development of a blue color confirmed the presence of nitrate residue. Due to its simplicity, this method was quickly accepted and ruled admissible evidence in court proceedings, even though it has shown that more than thirty substances (including cigarette ash, urine, rust, and fertilizers) gave false positive results.

As a result of numerous court challenges in the 1950's and 1960's, the "paraffin cast" test was ruled inadmissible as evidence. Harrison and Gilroy (1959) observed that metal components of bullet and primer materials such as barium, lead, antimony and copper are deposited on the firing hand after discharging a firearm. Even though the Harrison-Gilroy colorimetric spot test was suitable for laboratory determination of barium, antimony and lead, it was quickly found to be unsuitable to reliably distinguish between the "hand blanks" and metal deposits formed after discharging a weapon in actual firings. Nevertheless, the Harrison-Gilroy test demonstrated the need to quantitatively measure amounts of metals deposited on the hands.

In the early 1960's, neutron activation analysis (NAA) was shown to be suitable for trace determination of metals in gunshot residue (GSR). Initially, NAA was not widely accepted in forensic studies because only a few agencies were capable of performing time-consuming sample collection and processing. However, with the introduction of the cotton swab technique for sample collection (Hoffman, 1968; Goleb and Midkiff, 1974), NAA has become the leading method for the determination of elevated levels of barium, antimony and copper in GSR. The high cost of instrumentation, the need for highly skilled personnel, the long analysis time, and the limited availability of NAA to local law enforcement agencies suggested flameless atomic absorption spectroscopy (FAAS) as a viable alternative method for the detection of metals in discharge residue (Krishnan, 1974; Kinard and Lundy, 1975; Stone and Petty, 1974). Other analytical methods which have been used to detect metals and particles in GSR include photoluminescence (Jones and Nesbitt, 1975; Nesbitt, 1977), flame emission spectroscopy (Stone and Petty, 1974), soft X-ray radiography (Stone and Petty, 1974), and X-ray fluorescence (Wood and Methiesen, 1974). Recently, several groups used scanning electron microscopy (SEM) to detect

GSR particles (Andrasko and Maehly, 1977) and study the mechanism of GSR particle formation in order to distinguish them from their environmental sources of barium, lead and antimony.

Forensic science and crime laboratories around the world are in constant need for improved methods for crime scene evidence analysis. Specific and quantitative information is required by the investigator as rapidly as possible and since many determinations are not done on a routine daily basis, particularly in small, regional labs, the instrumentation should be inexpensive and easily maintained. To these ends, a method has been developed for determining metallic residues on the hands of suspected felons using the technique of anodic stripping voltammetry (ASV).

The ASV method has been shown to be a viable alternative to methods presently available such as common colorimetric tests (*e.g.* the Dermal Nitrate test and the Harrison-Gilroy color test) and the instrumental techniques of neutron activation analysis (NAA) and flameless atomic absorption (FAAS). ASV has been used for trace metal determination in a large number of applications. In GSR analysis the metals of primary importance are copper, lead and antimony. Though copper and lead are commonly found in trace amounts on all individuals, the amounts found on hands that have recently fired a handgun increase significantly from base values. Antimony, on the other hand, even in trace amounts, is indicative of probable contact with a handgun. The ASV technique provides simultaneous qualitative and quantitative information for these elements (see Figure 1).

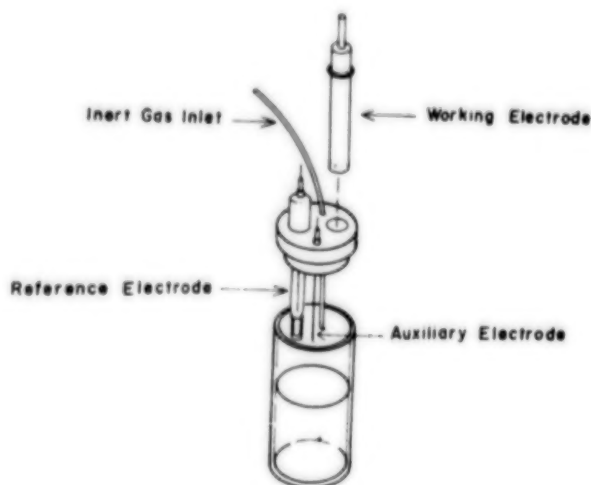


Figure 1. Electrochemical Cell for Anodic Stripping Voltammetry (ASV).



Some advantages of ASV are as follows:

- \* microgram-per-liter sensitivity
- \* freedom from optical interferences
- \* compatibility with high ionic strength solutions
- \* ability to determine valence states (speciation)
- \* capability for simultaneous multi-analyte determination (pattern recognition).

In the ASV procedure, metals are preconcentrated (reduced) from an electrolyte solution to a thin-film of mercury which has been deposited simultaneously on a carbon-based electrode (working electrode). The metals are then "stripped" (oxidized) from the mercury layer by changing the applied potential on the electrode. Since each metal has a characteristic potential at which it strips from the mercury layer and since the current required to remove the particular amount of metal from the mercury film is proportional to the original concentration, both qualitative and quantitative information can be obtained from a single experiment. The following procedure has been developed to apply the ASV technique to practical use as an investigational aid for the determination of the trace metals copper, lead and antimony in gunshot residue analysis.

#### RESIDUE SAMPLE COLLECTION PROCEDURE

Residue sample collection requires: (5) cotton-tipped plastic handled swabs in plastic vials for storage and transportation; 5% nitric acid solution in a squeeze bottle; (2) pair plastic disposable gloves.

Swab the appropriate area of the hands (right back, right palm, left back, left palm) with the cotton-tipped, plastic swabs that have been wetted with the 5% nitric acid solution. Note: The cotton swabs should not be touched without wearing the plastic gloves, and a new pair of plastic gloves should be used for each hand. Also make certain the plastic storage vials for the cotton swabs are appropriately labeled with the correct area of the hand swabbed and the control.

#### GSR ANALYSIS PROCEDURE

Reagents: 4M HCl solution containing 0.02M hydrazine sulfate; 0.01M  $\text{HgCl}_2$ . Equipment: CV-5 Bioanalytical Systems Voltammetry System. For this analysis, the initial potential on the CV-1B Controller should be set at  $-1.0\text{V}$ , the

anodic scan limit set to  $+0.1\text{V}$ , the scan rate at  $20\text{mV/s}$ , the scan direction switch toggled to the + (anodic) position (this is a momentary contact switch), and the filter set to 1 s. See the CV-5 manual for specific details on these adjustments. A GCE Glassy Carbon Working Electrode and RE-1 Silver/Silver Chloride Reference Electrode are used. Stirring is accomplished by a small magnetic stirrer placed under the voltammetry cell and a small teflon stirring bar (ca. 1 cm length)(see Figure 1). A digital voltmeter in the system aids in verifying voltages of stripping peaks.

#### Procedure

1. Remove the plastic handles from the cotton swabs with scissors.
2. Place the swab tip in a vial containing 4mL of the 4M HCl with hydrazine solution (Note: There are five samples in each residue analysis, four from the suspect's hands and one control). These samples are soaked for 1-3 hours, overnight if possible.
3. Mix (vortex) and transfer contents of the vial to the electrochemical cell (see Figure 1) and add 100  $\mu\text{L}$  of the 0.01M  $\text{HgCl}_2$  solution.
4. Place the small magnetic stirring bar in the electrochemical cell containing the sample solution.
5. Place the electrochemical cell in the cell compartment and insert the working and reference electrodes into the solution. Note: The glassy carbon working electrode should be polished and cleaned thoroughly before doing this analysis. Also check for air bubbles under the electrodes which can be removed by gently tapping the electrode body. Make certain the nitrogen tube is in place.
6. Bubble nitrogen through the solution for 180 seconds while stirring to purge dissolved oxygen.
7. Raise the nitrogen tube to just above the surface of the solution to provide an inner blanket of nitrogen during the actual analysis.
8. Apply  $-1.0\text{V}$  for 540 seconds with stirring followed by an additional 60 seconds without stirring.
9. With the recording paper in place and pen down, scan positive at  $20\text{mV/s}$  until the switching potential is reached ( $+0.1\text{V}$ ) at which time the function switch is flipped to

the HOLD position and the working electrode is turned OFF.

10. Clean the working electrode with deionized water and methanol following each run.

A typical voltammogram from gunshot residue is shown in Figure 2. Note the characteristic stripping potentials of each of the metals. The

amounts in each sample (Figure 2) are determined either by standard addition or by comparison with a calibration curve. Some typical test firing quantitative data for antimony are shown in Table 1. These data have been correlated with data from flameless atomic absorption spectroscopy.

**Table 1. GUNSHOT RESIDUE DATA (TEST FIRING) FOR ANTIMONY (Sb) IN MICROGRAMS ( $\mu\text{g}$ ) [RB = Right Back; RP = Right Palm; LB = Left Back; LP = Left Palm]**

Sample No.	Gun & Bullet	Condition	Sb ( $\mu\text{g}$ )			
			R-B	R-P	L-B	L-P
1	.38, 2" S&W w/w Super 38 Special	before shot	ND	ND	ND	ND
		after shot (outside)	27	15	ND	ND
		with right hand				
		after shot washed hand then handled gun both hands	10	66	18.2	92.8
2	.38, 2" S&W 38 Special	before shot	ND	ND	ND	ND
		after shot with right hand	25	32	ND	27
3	.38, 2" S&W	before shot	ND	ND	ND	ND
		after shot with right hand	35	15	12	ND
4	.357, 4", R&P	Indoor shot right hand	49	340	368	440
5	.38, 2" S&W R&P	Indoor shot right hand	74	65	34	280
6	.38, 2 1/2", S&W SW&P	Indoor shot	ND	138	ND	ND

ND—not detected

**Table 2. SUMMARY OF LC RESULTS ON A  $\text{C}_{18}$  REVERSE PHASE COLUMN.**

Compound	Detection Limits at S/N = 3	
	UV (2.54)	EC at -1.0V
HMX	1.5 ng	0.29 ng
Picric acid	0.47 ng	0.065 ng
RDX	0.88 ng	0.17 ng
Tetryl	0.77 ng	0.21 ng
TNT	0.65 ng	0.14 ng
Nitroglycerin	160 ng	0.38 ng
2,4-DNT	0.57 ng	0.16 ng
2,6-DNT	1.2 ng	0.17 ng
3,4-DNT	1.3 ng	0.15 ng
PETN	—	0.400 ng

Typical concentrations of antimony in gunshot residue analysis following this procedure are 10 to 40 ppb. Note that the linearity of the assay is limited to approximately 100–120 ppb (See Figure 3). If concentrations are above this value, the sample should be diluted and re-run. Quantitation of antimony can be accomplished by standard addition techniques or use of calibration curve.

## LCEC

Reductive and oxidative electrochemical detection with liquid chromatography can be applied to the determination of nitro aromatics, nitrate

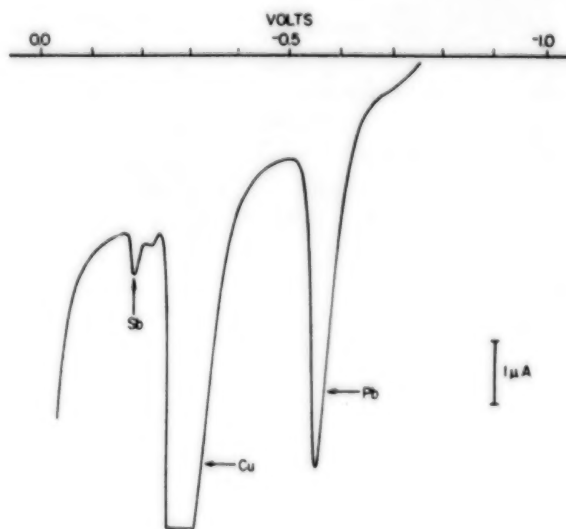


Figure 2. Typical Voltammogram of Gunshot Residue.



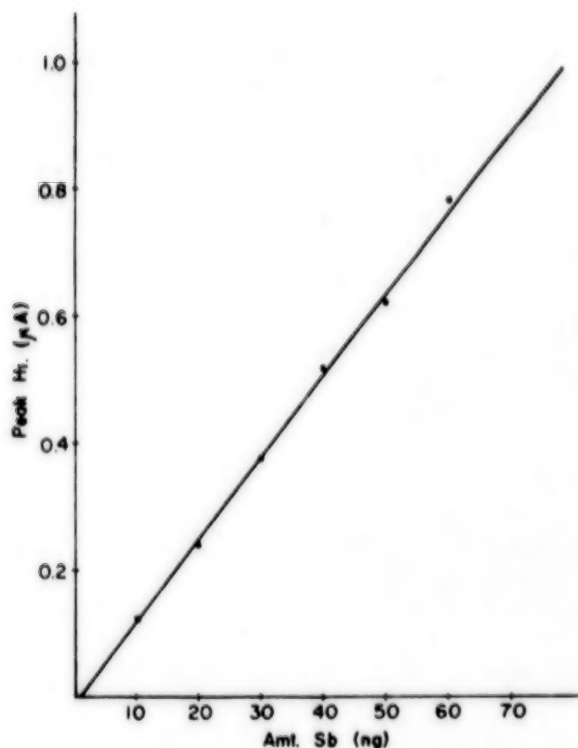


Figure 3. Calibration Curve for Quantitation of Antimony (Sb) from Hand Swabs.

esters, nitramines, and diphenylamines in military explosives and double base smokeless gunpowders. A sensitive and highly selective method is presented for the detection of organic (explosive) residue on individuals. The detection limits are of the order of 0.5, 1, 2, and 0.3 picomol for nitro aromatic, nitramine and nitrate ester explosive compounds, and diphenylamines, respectively.

In the last five years, oxidative mode electrochemical detection in liquid chromatography has become widely accepted for solving many problems of clinical, pharmaceutical, and environmental interest. Several reviews have been published on the advantages resulting from the combination of liquid chromatography with electrochemical detection (LCEC). Progress in reductive mode (LCEC) has been slow because of problems associated with dissolved oxygen, metal impurities, and the lack of reliable electrodes. Recent technological advances in detector design and the availability of more suitable electrode materials has generated a renewed interest in this technique.

This paper describes the application of reductive LCEC using glassy carbon and amalgamated gold electrodes (Au-Hg) to quantify explosive compounds in military explosives and smokeless

gunpowders, and the development of a highly sensitive and selective method for the detection of nitroglycerin, 2,4-dinitrotoluene (2,4-DNT) by reductive mode, and diphenylamine (DPA) by oxidative mode.

Chromatograms of common explosive mixtures such as nitroglycerin (Figure 4), COMP B (RDX and TNT), COMP C (RDX), C-4 (RDX), and Flex X (PETN) were investigated and typical chromatograms are shown in Figures 4 and 5.

Table 2 shows a comparison of U.V. detection and electrochemical detection. The compound nitroglycerin which is present in most smokeless powders offers a possibility for detection of gunshot residue on hand swabs as a comparison of nitroglycerin detector limits for U.V. vs LCEC (reductive) as LCEC is about 500X more sensitive than in U.V. detection. Preliminary work indicates nitroglycerin can be detected on hand swabs from test firing a handgun (.38 or .22).

#### EXPERIMENTAL (LCEC)

An LC-304T liquid chromatograph from Bio-analytical Systems equipped with an LC-300 solvent delivery system, Rheodyne 70-10 fixed volume (20 µL) rotary sample injection valve, LC-22

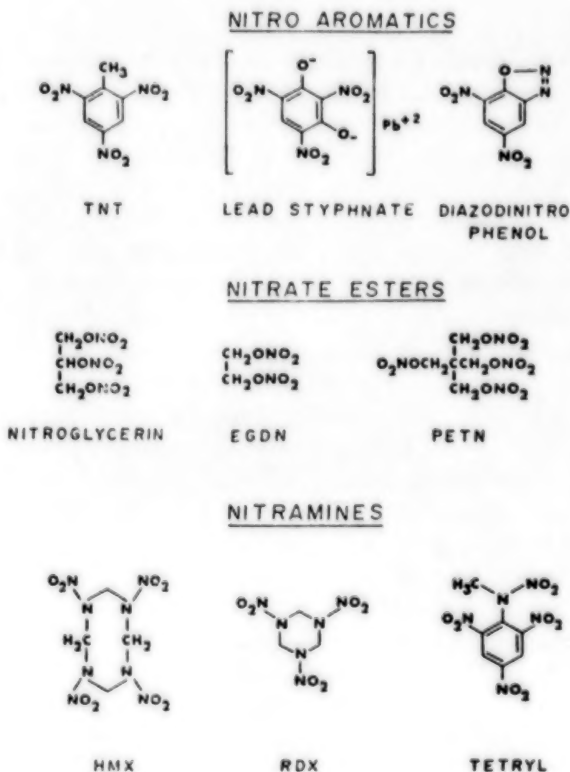


Figure 4. Typical Explosives.

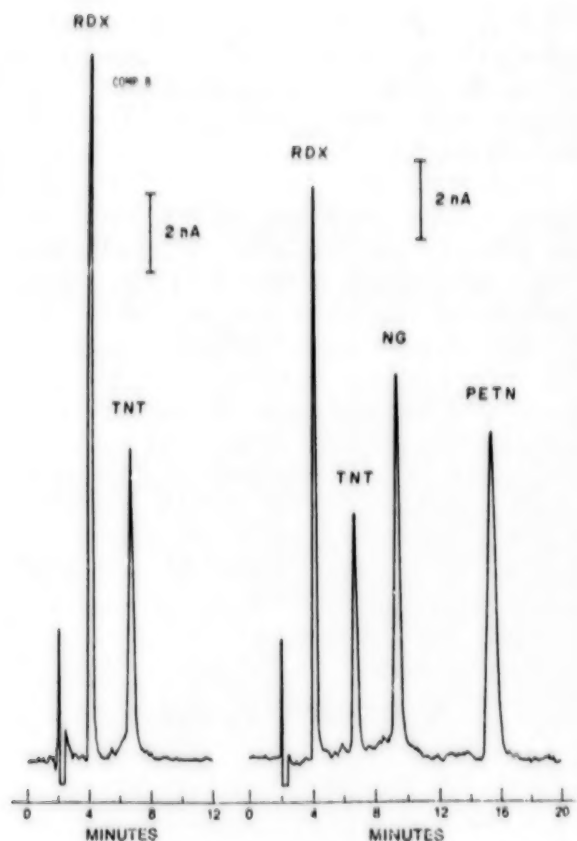


Figure 5. Mixture of Standard Explosives.

temperature controller, LC-23A column heating compartment, the LC-4A electronic controller and the LC-19 accessories package were used in all LC determinations. The LC column was a Biophase ODS 5 $\mu$  (25 cm). Spectrograde 1-propanol, triple distilled mercury, reagent grade anhydrous sodium acetate and monochloroacetic acid (all from Fisher Scientific) were used as purchased. All solvents for LC were filtered through 0.22  $\mu$ m Millipore filter (Millipore Corporation). Nitroglycerine (NG) was obtained as a mixture in lactose (10% w/w) from Purdue University Pharmacy, West Lafayette, IN, and used without further purification. The mercury film electrode was prepared by placing enough triple distilled mercury on the highly polished gold surface to cover the entire surface. After 2-3 minutes, the excess mercury was removed from the electrode surface using a computer card. MF-1 Microfilters with 0.2  $\mu$ m regenerated cellulose filters (RC58) were used to filter GSR sample solutions.

In summary, these procedures offer a unique approach to gunshot and explosive residue detection of both trace organic and metals. A useful

procedure is being developed to combine both of these analyses to the complex problem of GSR analysis in hopes of providing some useful data. The use of the dual electrode approach developed by Roston, 1982, should offer extended and more routine use of reductive LCEC as it eliminates many of the problems; mainly that of dissolved oxygen in both the mobile phase and the sample. A bibliography on both anodic stripping (ASV) and liquid chromatography with electrochemical detection (LCEC) is presented for informational use only.

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## EVALUATION OF FTIR AS A DETECTOR FOR THE HPLC ANALYSIS OF EXPLOSIVES

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**ABSTRACT.** HPLC has been used for some time, with a variety of detectors, for the identification of explosives. Unfortunately, the detector systems used with HPLC have lacked the necessary specificity for identification purposes. The examiner must use alternate techniques to confirm his findings. In analyses involving actual cases the examiner is often confronted with chromatograms that provide him with multiple peaks having retention times close to those of known explosives. Being able to distinguish contaminants from explosives using only these retention times is inadequate for identification. If a sensitive and specific detector system could be applied to each component as it is eluted, the need for additional confirmatory techniques could be eliminated. FTIR is such a detector. The use of HPLC coupled with FTIR as a detector is explored in this work, and its applicability to actual cases is evaluated.

### I. INTRODUCTION

The analysis of explosive residue using high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector offers high sensitivity, i.e., nanogram amounts of explosives can be detected, but suffers in its specificity. Consequently, there is a need for a detector that has specificity and still retains the high sensitivity of the UV-detector. In this study the Fourier Transform Infrared (FTIR) spectrometer is evaluated as such a detector.

FTIR analysis differs from conventional infrared (IR) analysis primarily in the speed of the analysis. Secondly, since many scans can be made within a short time period it is ideal for on-the-fly type of analyses such as the analysis of HPLC peaks. It can, also, offer higher sensitivity and resolution than conventional IR analysis. It should be noted that in general IR analysis provides sensitivity for sub-microgram amounts of many compounds.

In this study, the FTIR spectrometer coupled to a HPLC with a UV-detector was evaluated. The FTIR was used as a "confirmatory" or "more specific" detector of the eluting peaks. The FTIR can be used as an "on-line" or "off-line" detec-

tor. In the latter case the HPLC fraction is collected, stored, and concentrated prior to FTIR analysis.

### II. FTIR ANALYSIS OF BULK EXPLOSIVE

The explosives considered were 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), tetryl, and nitroglycerine. Potassium bromide micro-pellets were made of each explosive and the FTIR spectra obtained are shown in Figures 1 through 5.

The FTIR system used was an Analect FX-6250 instrument with the FXK-635 wideband HgCdTe detector assembly.

### III. HPLC ANALYSIS OF EXPLOSIVE MIXTURES

The HPLC system used was a Waters Model 6000 A Chromatographic Pump with a Model 441 Absorbance Detector. It was set at 214 nm for detection. The mobile phase was a mixture of 70% acetonitrile and 30% water. The flow rate 1 ml/min and the column was Waters C18 Radial Compression Module. Figures 6 and 7 show the HPLC separation of the explosives considered.



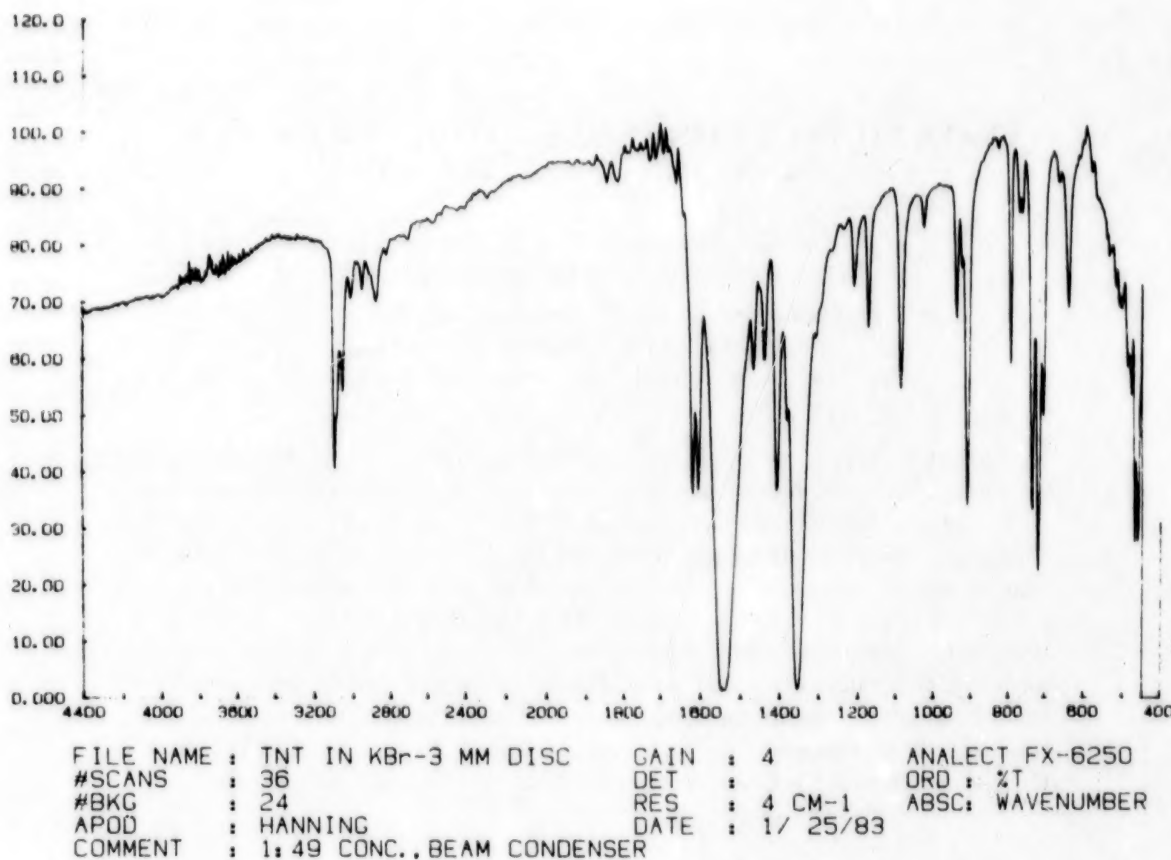


Figure 1. FTIR Spectra of TNT in KBr.

#### IV. THE COUPLING OF THE FTIR TO THE HPLC

The key device in the coupling of the HPLC with the FTIR is a flowthru cell with a beam condenser. The beam condenser is a Barnes Model 600 which claims to give a 16-fold increase in energy density. The flow-thru cell used is a Barnes demountable micro-flow-thru cell. This versatile cell can be assembled to give various pathlengths and corresponding cell volumes. The flow-thru cell is shown in Figure 8.

#### V. DETERMINATION OF THE OPTIMUM PATHLENGTH IN THE FLOW-THRU CELL.

First, we examined the FTIR spectra of TNT, PETN, RDX and tetryl explosives in the acetonitrile-water mobile phase. This being an aqueous system requires the use of cell windows insoluble in water. Cells of this nature are KRS-5 and Itran-2. We selected the KRS-5, because of its wider transmission range. The FTIR spectra of the explosives in this aqueous system were made using

the demountable flow-thru cell with beam condenser. The cell separation or pathlength chosen was 0.1 mm. This analysis did not require coupling to the HPLC. Figure 9 shows the FTIR spectrum of the aqueous system, i.e., the HPLC mobile phase of 70% acetonitrile and 30% water. In comparing these spectra to the pure explosives (Figure 1 to 5) one can see that there is considerable masking of many explosive peaks. Figures 10 to 13 show the spectra for TNT, RDX, PETN and tetryl, respectively. Each has the solvents removed as background, so theoretically, the resultant spectra are due mainly to the explosive. It should be noted that these spectra have a vertical scale expansion. The concentration of each explosive is 1000 ppm. The shaded peaks correspond to the explosive peaks that remain after the subtraction of solvent from explosive plus solvent.

Next the optimum pathlength had to be determined. Here TNT was chosen for this determination. Figure 14 gives the pathlengths available in the flow-thru cell and the corresponding cell volumes. The aperture used was the standard 3 mm.



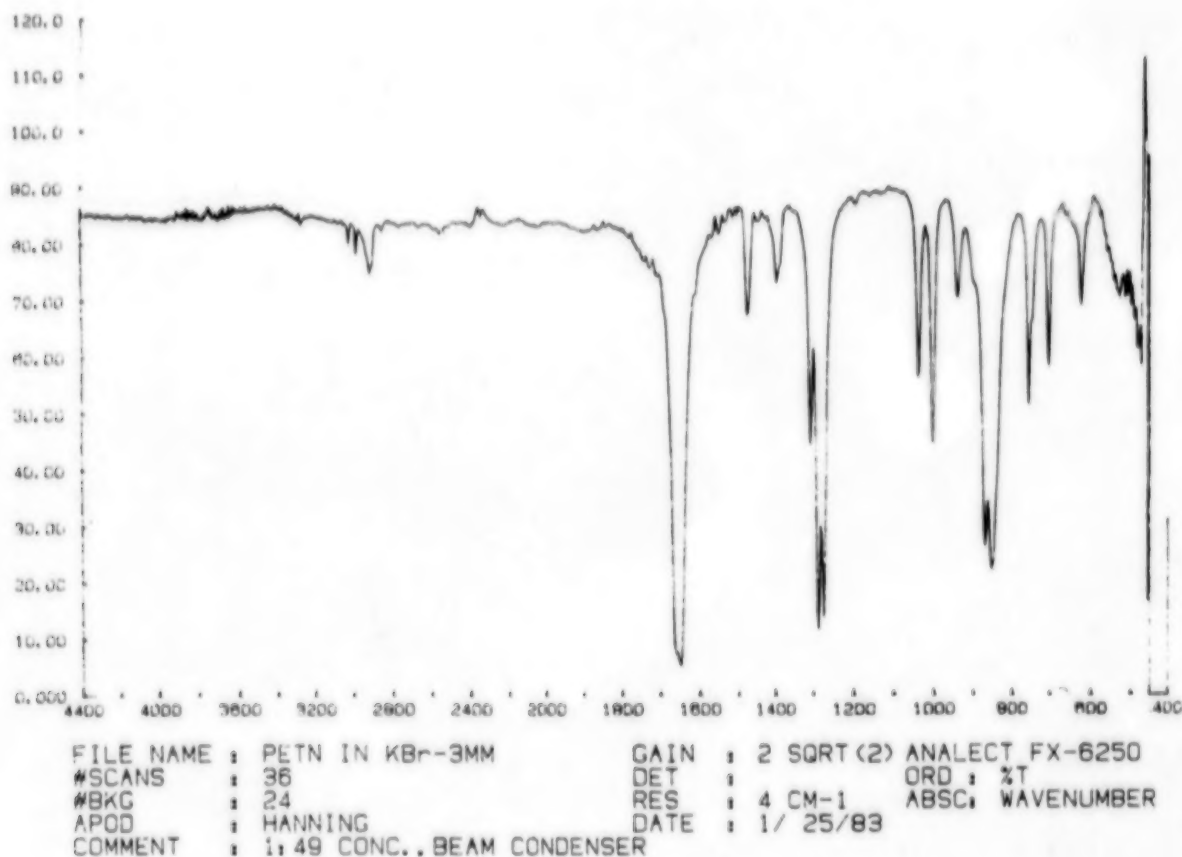


Figure 2. FTIR Spectra of PETN in KBr.

The concentrations considered for TNT were 1000 ppm, 500 ppm, 250 ppm and 125 ppm. Figure 15 gives the minimum amount (in nanograms) that was detected with each pathlength considered. The double line between the amounts detected for concentrations of 250 ppm and 125 ppm indicate that a concentration of 250 ppm is easily detected but not the concentration at 125 ppm. The interesting thing observed here is that as the cells' pathlength diminish and thus becomes more transparent to the HPLC mobile phase the minimal concentration detected does not increase as anticipated but remains the same. Therefore, the transparency of the mobile phase is increasing more rapidly than the decrease in concentration of sample due to the shortening of the cell pathlength.

#### VI. HPLC PEAK VOLUME vs MICRO-CELL VOLUME

From the conclusions reached by the optimum pathlength determination a pathlength between 0.015 mm to 0.1 mm permits 250 ppm to be detected. The absolute amounts detected are calculated

using the corresponding cell volumes. The amounts are between 32.5 and 250 ng for a concentration of 250 ppm.

The remaining question is what minimal quantity of explosive must be present in the eluant peak delivered by the HPLC to the FTIR in order for the FTIR to detect it. The answer is not very encouraging. In Figure 16 an equation is developed for relating the weights of explosives in the HPLC peak volume and in the micro-cell. It is based on the simplified model of the peak volume being uniform in concentration.

Considering an average peak volume of 300  $\mu$ l, the amount needed from the HPLC at a concentration of 250 ppm is 75  $\mu$ g. (Figure 17). Clearly, this is not as sensitive as the UV-detector but does offer more specificity.

#### CONCLUSION

This work has focused on optimizing the flow-cell pathlength in order to detect an explosive peak in the HPLC mobile phase. The second phase was to establish lower limits of detection for

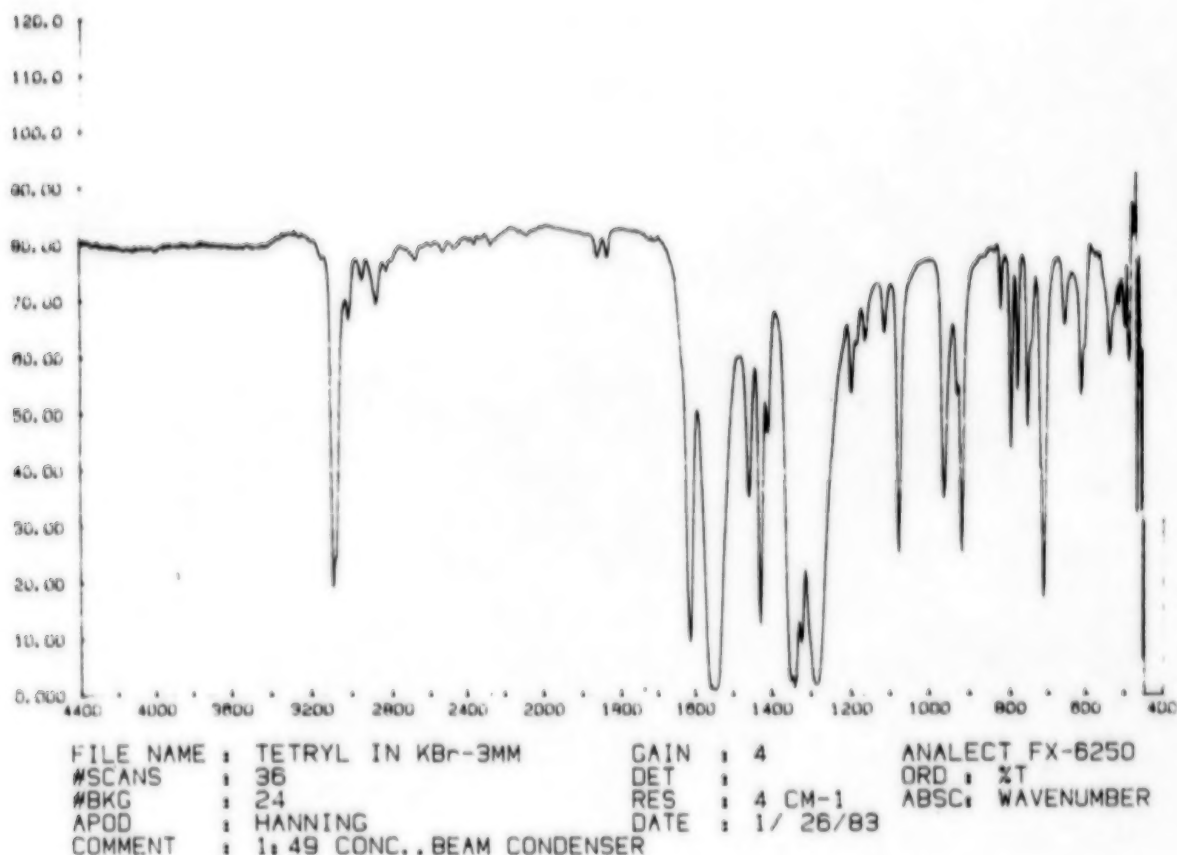


Figure 3. FTIR Spectra of Tetryl in KBr.

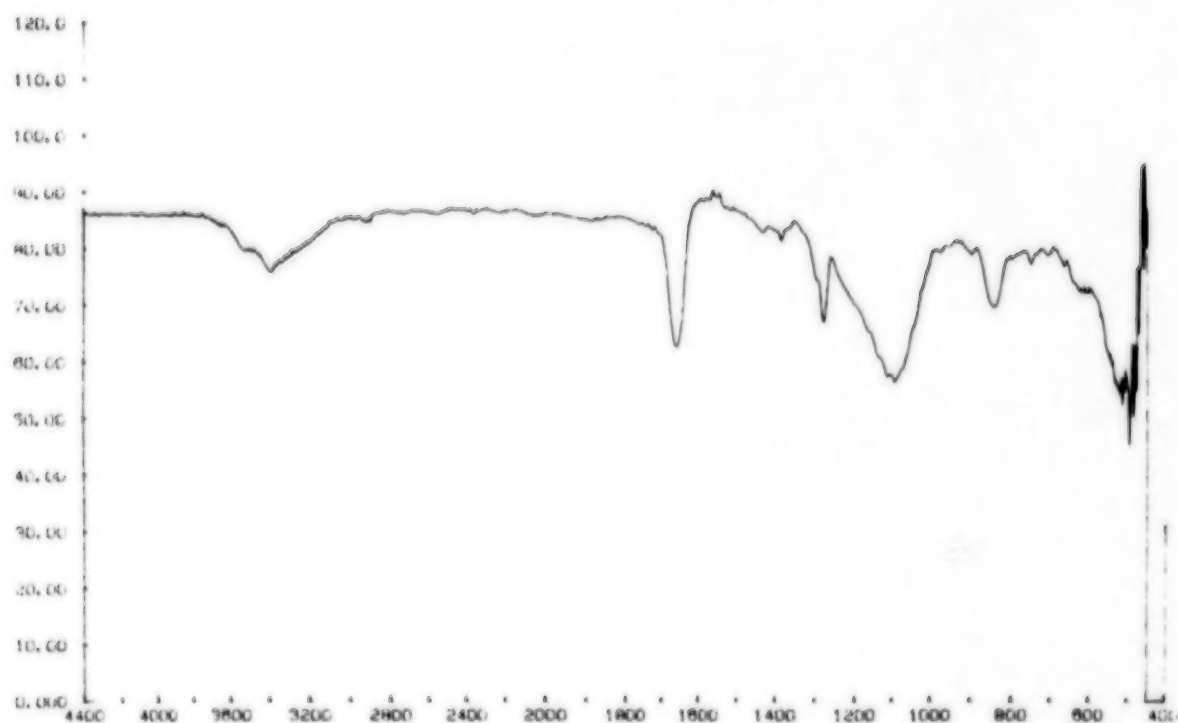
the explosive within the cell. After optimizing the flow-cell size in order to detect the explosive it became apparent that the concentration of explosive in the HPLC eluant would not be sufficient for detection. In order to overcome this a larger (longer pathlength) volume cell would have to be used. But as was seen in the experiment an increase in cell size produced an increase in the HPLC mobile phase which made the cell less transparent.

The method does not allow for a small quantity of material (explosives) to be identified in a large amount of IR absorbing solvent. The fine details of the IR spectra necessary for compound identification are obscured. Only the major bands of the

explosives can be seen. While not providing sufficient information for positive identification they do provide additional information to that provided by the UV-detector. The method at this point does not lend itself to on-the-fly analysis. A future possibility, when using this type cell would be to find a more IR transparent HPLC solvent system.

#### ACKNOWLEDGEMENT

The authors thank Miss Lisa Wellington, an intern from the Forensic Science Undergraduate Program at the University of Central Florida, Orlando, FL, for assisting us in this project.



FILE NAME :	NG XT: ACETONE	GAIN :	4	ANALECT FX-6250
#SCANS :	36	DET :		ORD : %T
#BKG :	24	RES :	4 CM-1	ABSC: WAVENUMBER
APOD :	HANNING	DATE :		
COMMENT :	3MM DISC. 3 TABS (START)			

Figure 4. FTIR Spectra of Nitroglycerine in acetone.

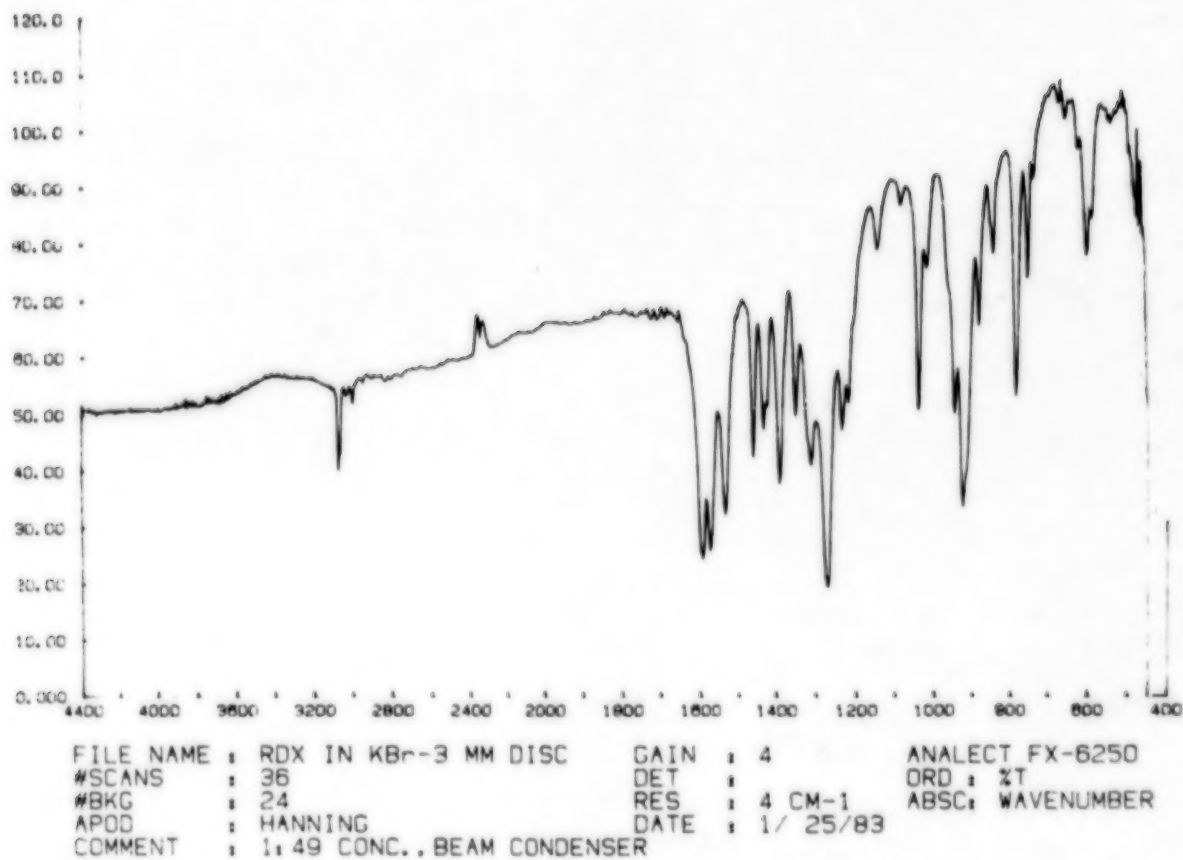
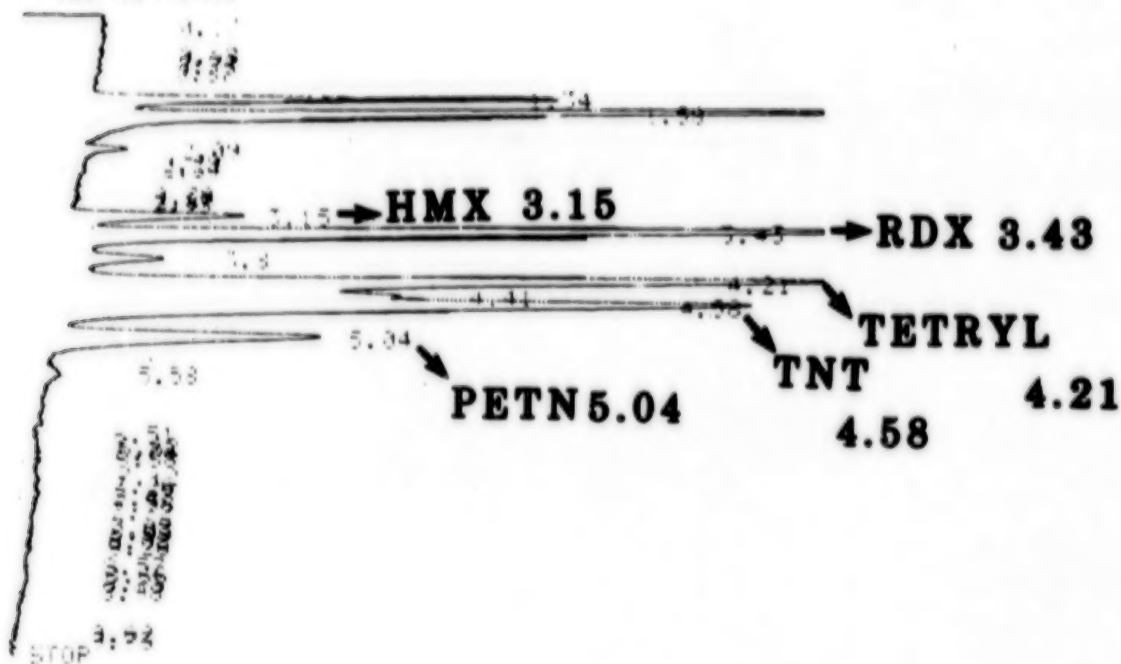


Figure 5. FTIR Spectra of RDX in KBr.

20  
 14.140N  
 0.1405  
 02.10.13.48.

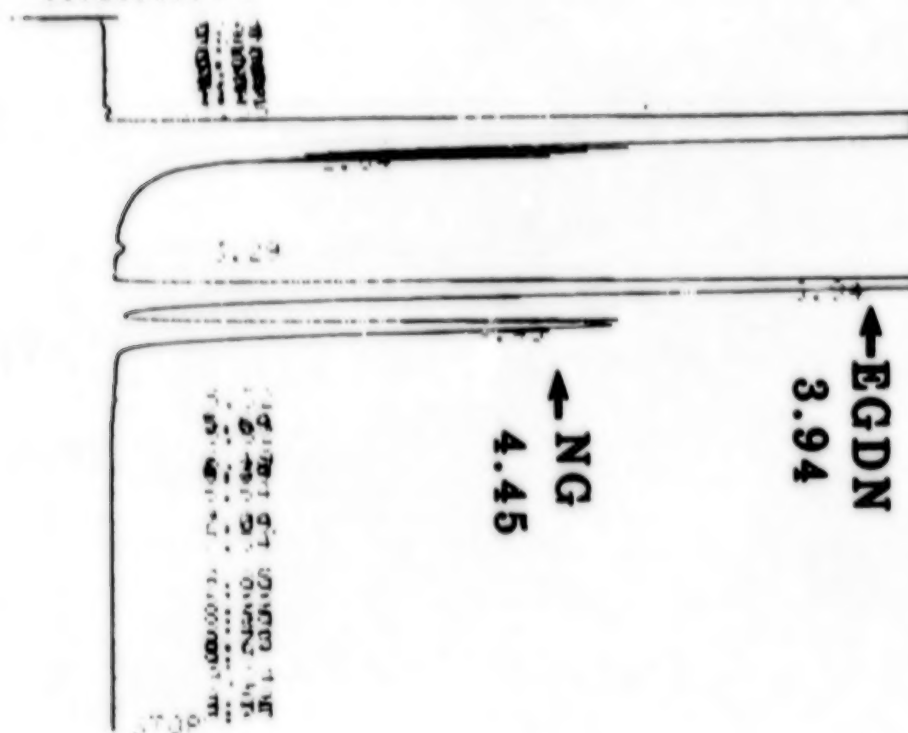


1-114  
 SNPL # 00  
 FILE # 114  
 METHOD 41

#	NAME	TIME	CONC	AK	AREA
1		1.34	5.1069		3014
2		1.58	5.4692		3134
3		3.15	5.4635		1712
4		3.43	19.806	V	4776
5		3.8	2.3763	V	1173
6		4.21	20.0209	V	4883
7		4.41	5.2441	V	2588
8		4.58	19.0354	V	4796
9		5.04	1.4521		2678
	TOTAL		99.4999		14563

Figure 6. HPLC separation of HMX, RDX, Tetryl, TNT and PETN.

10.000 STANDARD  
 10.000 1000 1.0000  
 10.000 10.000 10.000



10.000  
 10.000  
 10.000  
 10.000  
 10.000

#	NAME	TIME	AREA	%	AREA
1		1.79	14.3578	7	170639
2		3.94	4.3577	7	1724
3		4.45	4.4458	7	18190
4		5.29	5.2084	7	10534
	TOTAL		49.9999		201088

Figure 7. HPLC separation of NG, EGDN.





## Micro Flo-Thru Cell

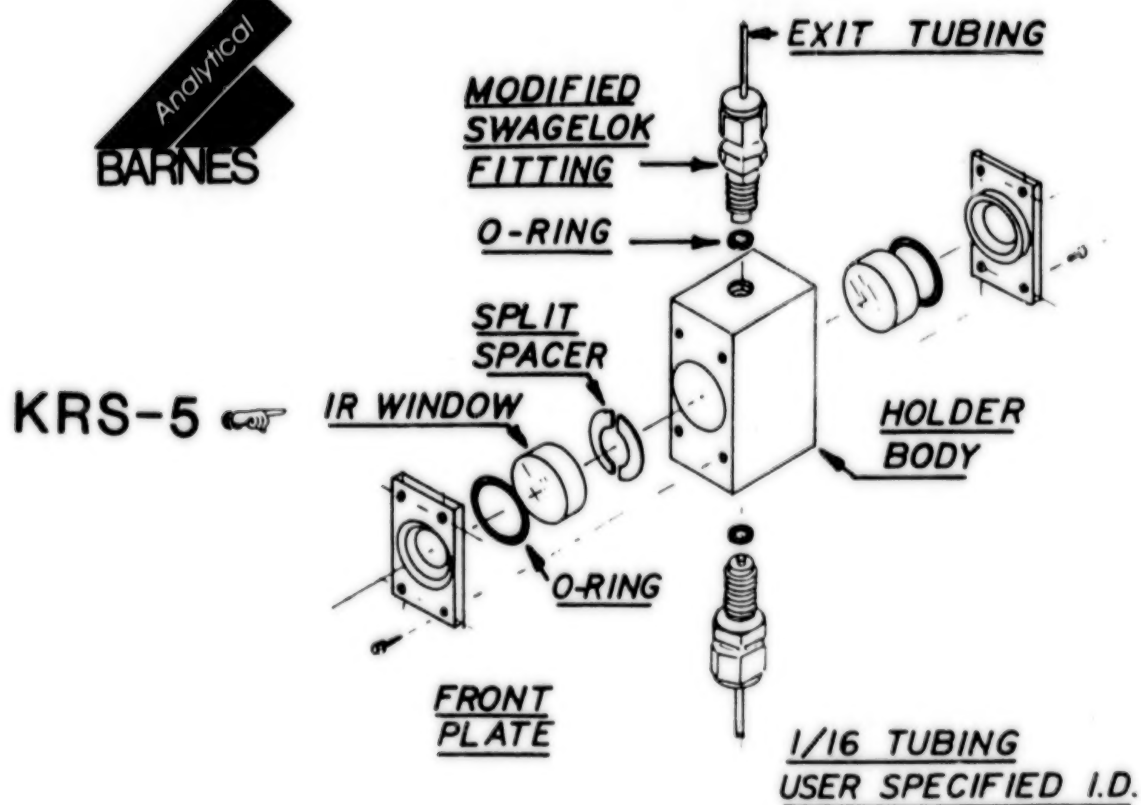


Figure 8. Barnes Micro Flo-Thru cell.

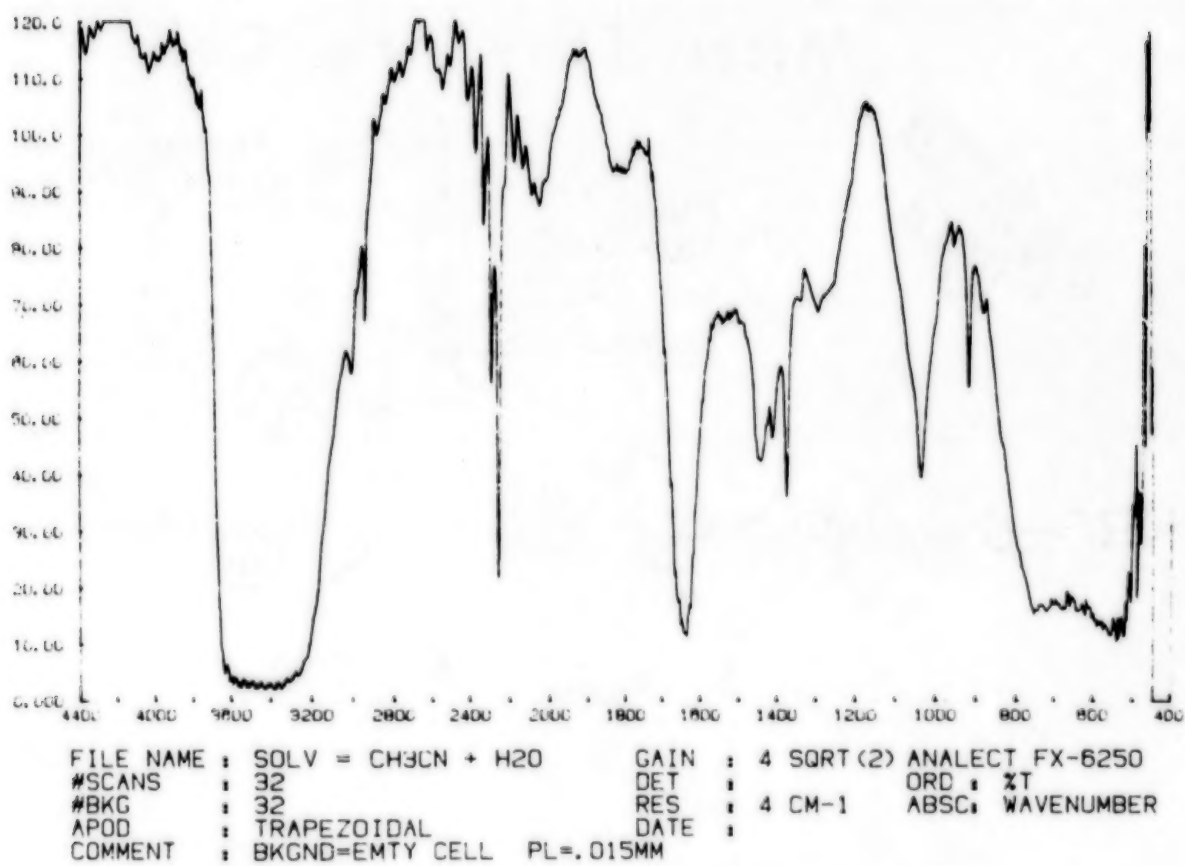


Figure 9. FTIR Spectra of the HPLC mobile phase; 70% Acetonitrile and 30% HOH.

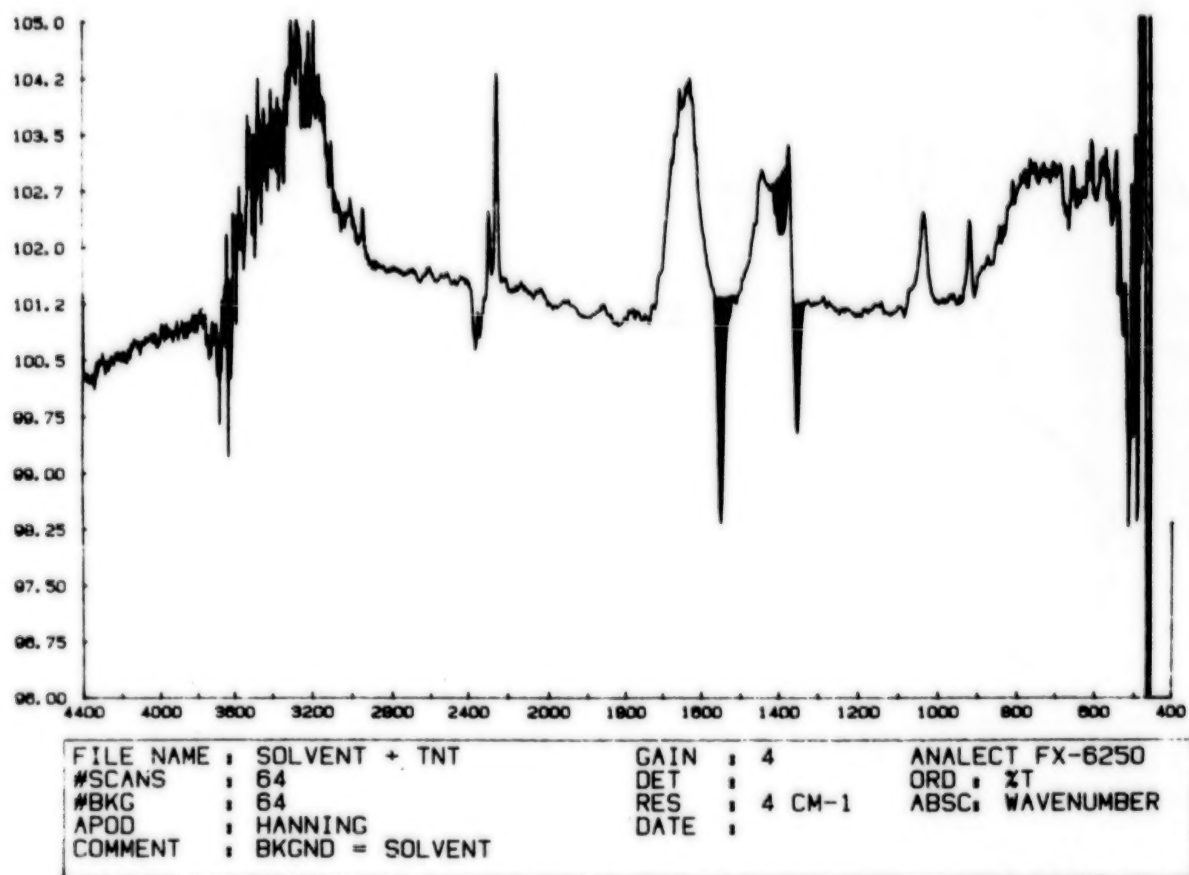


Figure 10. FTIR Spectra for TNT after subtraction of HPLC mobile phase spectra.

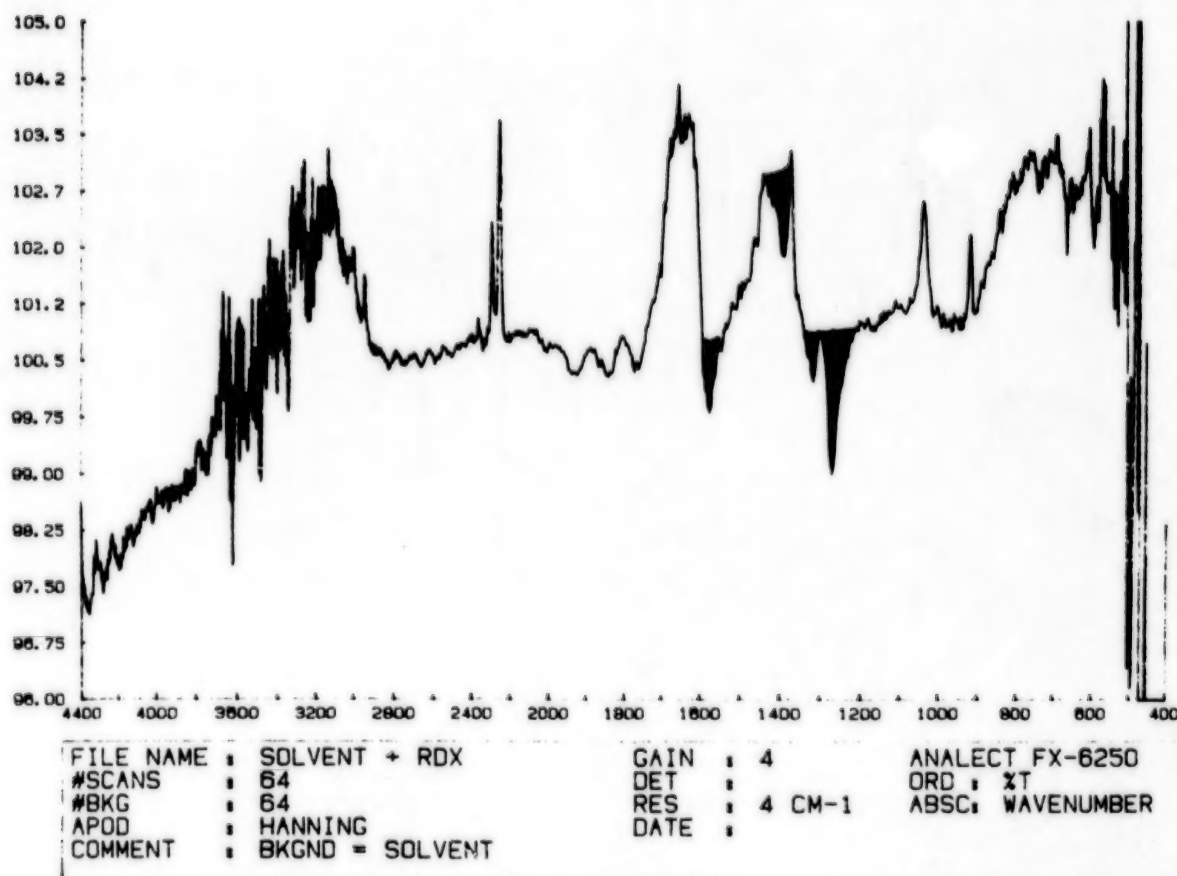


Figure 11. FTIR Spectra for RDX after subtraction of the HPLC mobile phase spectra.

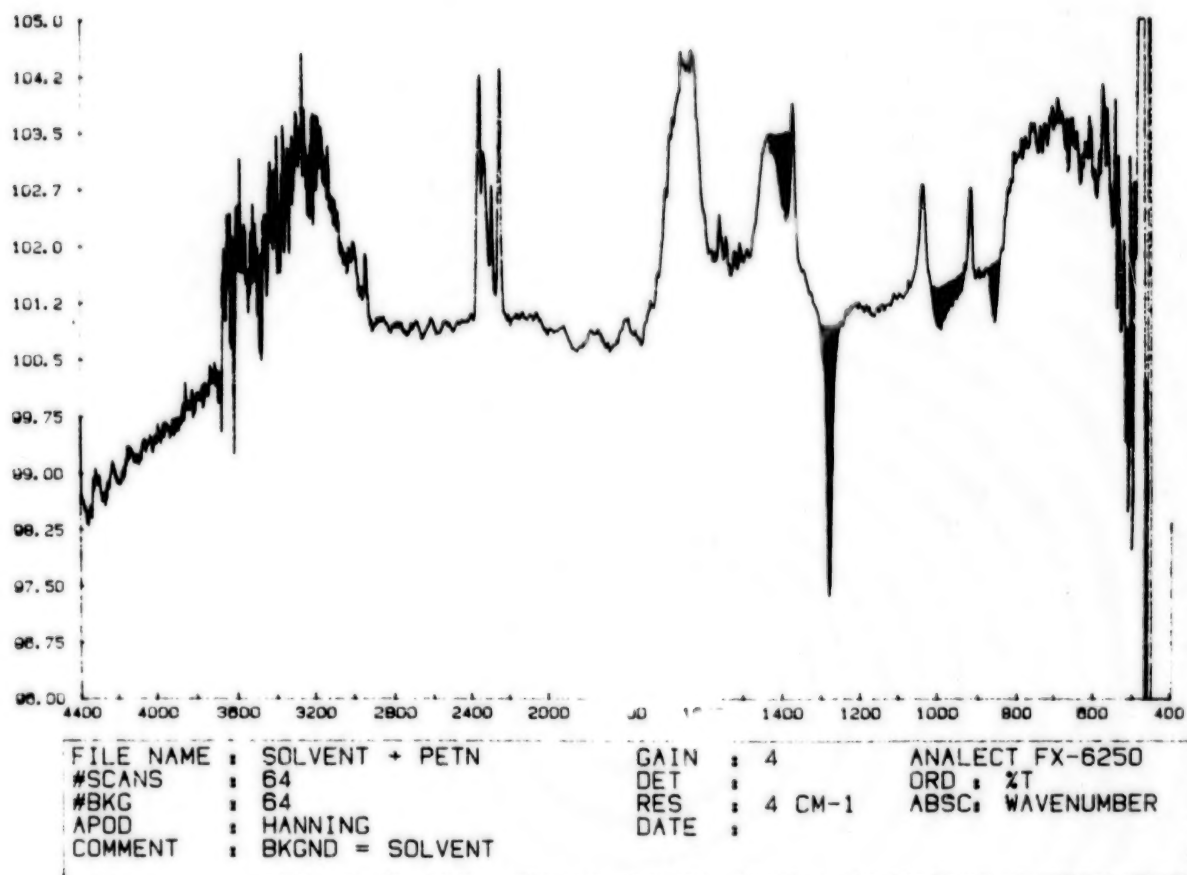


Figure 12. FTIR Spectra for PETN after subtraction of the HPLC mobile phase spectra.

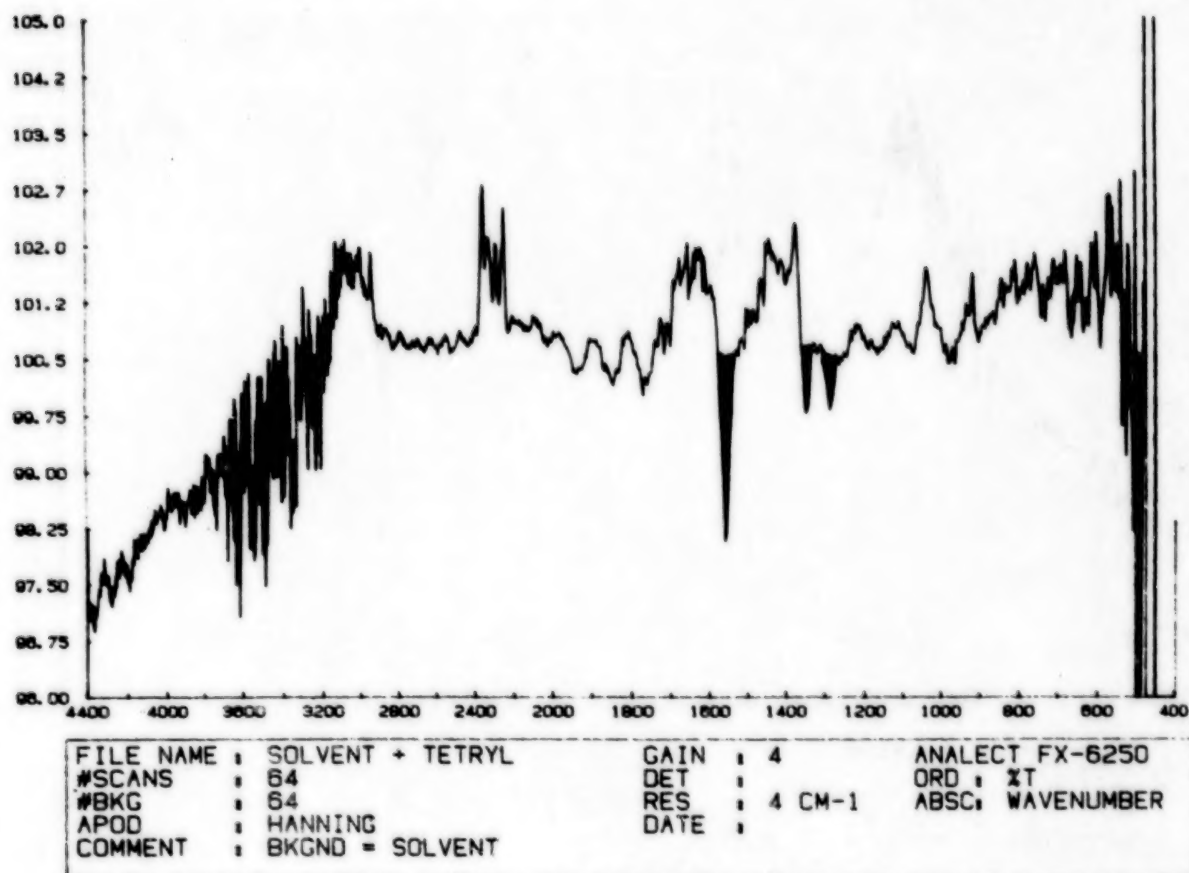


Figure 13. FTIR Spectra for Tetryl after subtraction of the HPLC mobile phase spectra.



# OPTIMUM PATHLENGTH

## B. PATHLENGTHS (CELL VOLUMES) CONSIDERED

Pathlength (mm)	.015	.025	.05	.10	.20	.50	1.0
Volume (μl)	.15	.26	.51	1.0	2.0	5.1	10.1

3mm Aperture for standard Spacers

Figure 14. Available pathlengths and cell volumes considered.

# OPTIMUM PATHLENGTH

## D. MINIMUM AMOUNT (IN ng) DETECTED PER EACH PATHLENGTH

Pathlength (mm)	.015	.025	.05	.10	.20	.50	1.0
Volume (μl)	.15	.26	.51	1.0	2.0	5.1	10.1
Conc	1000 ppm	150	260	510	1000		
	500 ppm	75	130	255	500		
	250 ppm	37.5	65.0	128	250		
	125 ppm	18.8	32.5	63.8	125		

Figure 15. Optimum pathlength. Minimum amount (in ng) detected per each pathlength.

# HPLC PEAK VOLUME -vs- MICRO CELL VOLUME

V = Peak Volume

A = Weight of Explosive in Peak Volume



v = Cell Volume

a = Weight of Explosive in Cell

$$A = a(V/v)$$

Figure 16. Development of an equation relating explosive weight in a given HPLC peak volume to cell volume and weight in the cell.

# HPLC PEAK VOLUME -vs- MICRO CELL VOLUME

... CONTINUED

AVERAGE PEAK VOLUME V = 300 μl

Pathlength (mm)	.015	.025	.05	.10	A
v = Volume (μl)	.15	.26	.51	1.0	
Conc.	1000 ppm	150	260	510	1000 300 μg
	500 ppm	75	130	255	500 150 μg
	250 ppm	37.5	65.0	128	250 75.0 μg
	125 ppm	18.8	32.5	63.8	125 37.5 μg

a(ng)

Figure 17. Table relating cell pathlength, cell volume and explosive concentration.

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## **MISCELLANEOUS METHODS**



## FORENSIC COMPARISON OF EXPLOSIVE SAMPLES BY PROTON MAGNETIC RESONANCE SPECTROMETRY

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**ABSTRACT.** Qualitative and quantitative determination of significant by-products and trace impurities is useful as additional forensic information to differentiate between materially equal explosive compounds originating from different sources. For this purpose chromatographic techniques (especially HPLC) and nuclear magnetic resonance are used. An example of the application of NMR-spectrometry for the rapid and simple characterization of organic explosives is demonstrated. The detection of low levels of a specific impurity (trinitroanisole) in trinitroaniline samples allows comparative analysis and also the establishment of relevant connections. Furthermore, the NMR-analytical identification of this characteristic explosive impurity furnishes indications concerning the manufacturing process.

The analysis of explosives and of their residues after explosions carried out by means of a wide variety of chemical and physical examination methods has been repeatedly studied and was subject of many scientific publications. Moreover, it is above all the determination of small quantities of additives or impurities that frequently leads to a differentiation of homogenous explosives of different origin. Such distinctive features may be conditioned by different manufacturing processes, admixtures of additives, the utilization of starting material of varying quality, but also by variations between the individual charges as well as aging or climate influences (heat, moisture) and other factors. This additional analytical information concealed in the sample often facilitates a better specification of the proof by forensic science and, thus, enables the forensic comparison of samples or even existing leads to links between crime cases.

A successful analysis of such significant additives or impurities or the "fingerprinting" of explosives is achieved on the one hand by means of various chromatographic techniques, especially by High Pressure Liquid Chromatography (HPLC) [Krull and Camp, 1980] and on the other hand

above all by means of Nuclear Magnetic Resonance Spectrometry (NMR) [Schiele and Vordermaier, 1982].

The presence of impurities, additives, etc. in a substance to be examined may be recognized in the NMR spectrum by the occurrence of additional resonance signals or—in case of superposition—by non stoichiometric proportions in the integration. The signal areas are proportional to the relative number of the related hydrogen atoms and, thus, reflect the extent of impurity involved, whereas chemical shifts, multiplet structures and intensities allow to draw conclusions as to the kind of impurity given in the individual case. Thus, NMR spectrometry renders possible the simple and quick simultaneous presentation of specific impurity patterns as well as mixtures of organic explosives constituents. Let us illustrate this by a practical example:

Recently, an about 80-year-old pensioner was suspected, in spite of his old age, to occasionally supply against payment anarchist circles with explosives. When his weekend house was searched, chemicals were found as well as detonators, wires and tools of older design which are appropriate for the manufacture of explosive devices (Figure 1). Furthermore, traces were found and preserved

\* Dr. Ing., Chemist, Forensic Science Laboratory

\* \* Dr. rer. nat., Chemist, Forensic Science Laboratory



Figure 1. Seized chemicals and tools used to manufacture explosive devices.

in the surroundings of the secluded house which raised the suspicion that presumably test explosions had been made there a short time before.

During forensic examination of the exhibits the interest was soon concentrating on a yellow substance similar to picric acid which had been seized in powdered form, but also in pressed bars and partly mixed with potassium nitrate and other inorganic substances. By IR- and  $^1\text{H}$ -NMR spectro-metric methods it was possible to quickly identify this chemical as 1 - amino-2,4,6-trinitro-benzene (trinitroaniline, TNA, picramide). Trinitroaniline which is produced by reaction of trinitrochloro-benzene with ammonia or nitrating of nitraniline has found but little application as an explosive in former times, however, was used during World War II to a limited extent and mostly mixed with TNT. Nowadays, it seems that it has almost no significance anymore as an explosive.

In the proton magnetic resonance spectrum of trinitroaniline (Figure 2b) appears the intensive clear-cut singlet of two protons at the six-membered ring in the expected region of trinitro-substituted aromatic compounds and is superimposed by a broad, strong down field shifted signal of the amino group. In the sample spectrum (Figure 2a) two additional small signals at 9.08 and 4.18 ppm appear which, according to  $^1\text{H}$ -NMR analysis are to be allocated to the chemical substance 2,4,6-trinitroanisole (Figure 2c). From the relation of the integrated signal area the portion of this additive to approximately 2.5 mol% may be calculated. It is characteristic that these impurity signals-in comparable percentage-are detected in all TNA-containing exhibits pertaining to the crime case concerned, also in the cut samples.

The provenance of the slight share of trinitro-anisole (on account of its sensitiveness to hydroly-



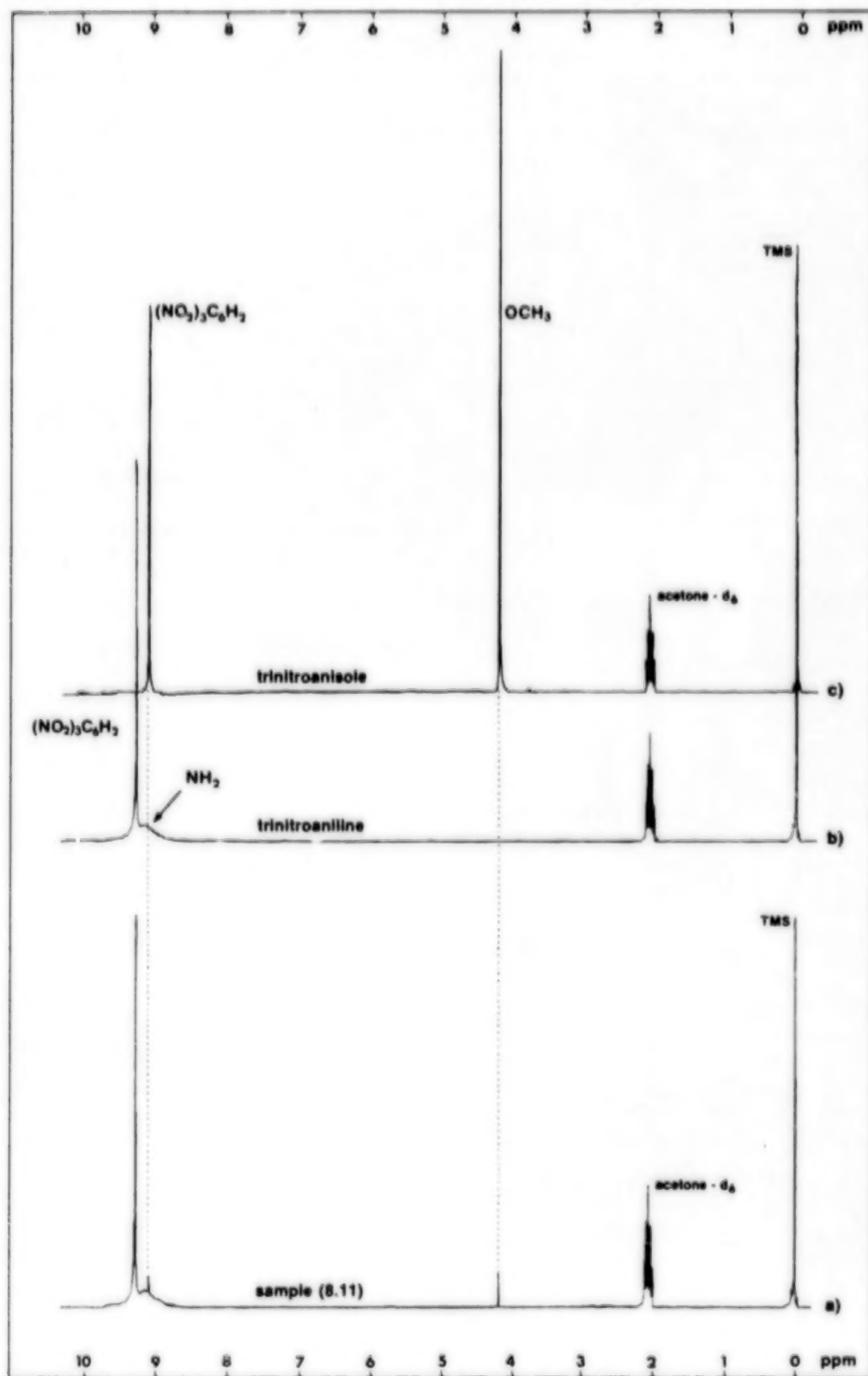


Figure 2. Proton NMR spectra

sis and its toxicity virtually meaningless as an explosive agent) seems at first sight unclear. However, comprehensive literature research furnished indications that—differing from the usual, above-described manufacturing process—trinitroaniline was in former times partly also prepared out of trinitroanisole (Figure 3). This would imply that this specific "marker" results from the manufacturing process and can be attributed to chemically unchanged starting material.

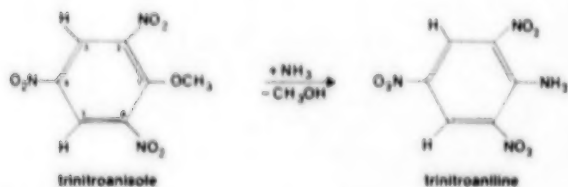


Figure 3. Former synthesis of trinitroaniline via trinitroanisole.

In our above-mentioned example a date of manufacture can be deduced from the results of the analysis of the examined TNA-sample that lies in a rather remote past. This fact corresponds to the old age of the suspect and the rest of the seized evidence.

Spectrometer:	Fourier NMR-
system:	Spectrometer
	BRUKER WH 90
Data System:	ASPECT 2000
	Computer with
	High Density
	Floppy Disk System

NMR-Solvent:	Acetone—d <sub>6</sub>
Standard	Tetramethylsilane
(int.):	(TMS)

## SUMMARY

Qualitative and quantitative determination of significant by-products and trace impurities is useful as additional forensic information to differentiate between materially equal explosive compounds originating from different sources. For this purpose chromatographic techniques (especially HPLC) and Nuclear Magnetic Resonance are used.

An example of the application of NMR-spectrometry for the rapid and simple characterization of organic explosives is demonstrated. The detection of low levels of a specific impurity (trinitroanisole) in trinitroaniline samples allows comparative analysis and also the establishment of relevant connections. Furthermore, the NMR-analytical identification of this characteristic explosive impurity furnishes indications concerning the manufacturing process.

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# **RADIOFREQUENCY RESONANCE ABSORPTION SPECTROSCOPIC (RRAS) METHODS FOR THE DETECTION AND ANALYSIS OF EXPLOSIVES**

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**ABSTRACT.** The field of radiofrequency resonance absorption spectroscopy (RRAS) comprises the techniques of nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), and electron magnetic resonance (EMR), all of which are useful in the detection and qualitative and quantitative analysis of explosives. Each of these techniques can be used on some but not all explosives. Hydrogen NMR signals can be obtained with good signal-to-noise ratio from all explosives except black powder. Nitrogen NMR signals are also available from many explosives. Nitrogen NQR spectra can be obtained from a few explosives. Free electron EMR responses are available from those explosives containing pyrolyzed materials. Each of these techniques will be briefly described, their expectations compared, and some results, from many years of measurement experience, displayed.

## **I. BACKGROUND**

Southwest Research Institute has been making nuclear magnetic resonance measurements on explosives and propellants since 1956, and developing specialized magnetic resonance equipments for performing specific measurements on propellants and explosives since 1958. From 1958 to 1960, two equipments were developed for Thiokol Corporation to measure the concentrations of aluminum and hydrogen in a solid propellant mixture just before it is poured in the casing. From 1964 to 1970, a moisture meter for black powder and M-10 propellant was constructed for Picatinny Arsenal. From 1968 through 1970, a magnetic resonance device was made to measure the amounts of water and nitric acid in the three-part mixed acid of a nitrating plant producing TNT and nitrocellulose. By subtraction, the amount of sulfuric acid was determined. From 1973 through 1977, a magnetic resonance device was constructed to detect explosives hidden in the ground. From 1976 to the present, magnetic resonance devices have been constructed to detect explosives hidden in letters, baggage and large containers. During these equipment developments, nuclear magnetic resonance measurements

have been made on many types of explosives and propellants, and many other applications for qualitative and quantitative analyses have been indicated. Some of these application possibilities will be described in the next section, followed by a brief description of the magnetic resonance phenomena and a discussion of the information which can be obtained from the magnetic resonance signals from some explosives and propellants. The last section will give brief descriptions of some of the instrument manifestations which are possible.

## **II. NMR APPLICATIONS TO EXPLOSIVES AND PROPELLANTS**

Many NMR measurements have already been performed at SwRI on explosives and propellants. These will be discussed in Section IV. The data from these measurements have led to the following conclusions:

(a) The hydrogen NMR signals from solid explosives have very short values of  $T_2$  (7 to 50 microseconds) and very long values of  $T_1$  (3 to 300 seconds at 3.0 MHz).

(b) Solid explosives such as RDX and TNT have strong spin-spin coupling between the hydro-

gen and nitrogen nuclei when the hydrogen NMR resonating frequency is made equal to the nitrogen-14 nuclear quadrupole resonance frequency.

(c) The hydrogen NMR signals from the liquid components of explosives and propellants including moisture, have longer values of  $T_2$  (1 to 200 milliseconds) and much shorter values of  $T_1$  (1 to 200 milliseconds) than do the solid components.

(d) Useful signal/noise ratios are obtained for the hydrogen transient NMR signals from the high concentration components of the solid explosives and propellants with magnetic fields of from 500 to 1000 Gauss.

(e) Useful signal/noise ratios for low concentration liquid materials such as moisture with longer values of  $T_2$  may require a higher magnetic field for an accurate measurement, perhaps as high as 7000 Gauss, or a hydrogen resonance frequency of around 30 MHz, for concentrations of from 0.1 to 1 percent.

(f) The charcoal used in black powder and as a coating on some propellants gives a strong free electron magnetic resonance signal.

The above conclusions have indicated several measurement possibilities using hydrogen transient NMR signals. Among these possibilities are:

(a) Constituent quantitative analyses can be made in explosives and propellants in their solid form. The types considered have been: Composition B, Composition A, Composition C, detonator mixtures such as M-55, and RDX (HMX concentrations).

(b) Solid/liquid ratios in flowing slurries of materials such as TNT and Composition B as well as the RDX and TNT concentrations can be determined.

(c) Moisture measurements can be made in fixed samples and flowing streams up to one inch I.D. for all explosives and propellants.

(d) The hydrogen NMR signal from the incompletely pyrolyzed hydrocarbon material in charcoal can be used as a quality control to measure the amount of pyrolyzation.

(e) The hydrogen NMR signal from the incompletely pyrolyzed hydrocarbon material and from the moisture can be used to give a non-weighing determination of the moisture in black powder and in the charcoal as a raw material.

(f) The free electron magnetic resonance signal from charcoal can also be used as a quality control measurement on it as a raw material.

(g) The free electron signal can be used in com-

bination with the hydrogen NMR signal from the water to make a non-weighing measurement of percent moisture in black powder if there is no hydrogen signal from the incompletely pyrolyzed hydrocarbon in the charcoal.

### III. THE PHENOMENA OF MAGNETIC RESONANCE

Magnetic resonance is a type of absorption spectroscopy involving the resonance absorption of electromagnetic energy caused by the interaction of the magnetic moments of nuclei or free electrons with a magnetic bias field. Not all nuclei and electrons have magnetic moment. Nuclei have a magnetic moment when they have even-odd or odd-even combinations of protons and electrons. Thus, hydrogen-1, oxygen-17 and carbon-13 nuclei have magnetic moment; oxygen-16 and carbon-14 nuclei do not. Electrons have a magnetic moment only when they are single and free. Pairs of electrons, in orbit for example, pair by the Pauli pairing principle to produce no net magnetic moment.

Without the magnetic bias field, there are no resonant absorption frequencies. When nuclei and electrons with a magnetic moment are placed in a bias magnetic field, the nuclei and electrons are established in an energy absorbing condition at an exponential rate whose time constant is  $T_1$ . In five time constants, essentially all of the nuclei or free electrons are biased for energy absorption and they are in thermal equilibrium with their surroundings called the lattice. Values of  $T_1$  range from tens of nanoseconds to thousands of seconds over most of the ranges of nuclei, free electrons, and material property variations. When electromagnetic energy is fed into these biased nuclei or free electrons, in the proper direction, at the proper frequency and of the proper magnitude, the biased nuclei or free electrons will absorb energy and become out of thermal equilibrium with their surroundings. When out of thermal equilibrium with their surroundings, energy will flow from the nuclei or free electrons to the surroundings exponentially at a rate of  $T_1$ . If energy is fed in at a rate faster than the nuclei or free electrons lose energy to the surroundings, they, in time, become saturated. When the energy is fed in at a lower rate than it is lost, energy will continue to be absorbed by the nuclei or free electrons and the rate of energy absorption is proportional to the volume concentration of nuclei or free electrons. Therefore, a quantitative analysis can be performed be-

low saturation. When energy is fed in continuously at a level either below or above saturation, the technique is called the steady-state technique.

A transient technique can also be used where the radiofrequency energy is pulsed. It was found that at equilibrium, the hydrogen nuclei or free electrons are aligned parallel and antiparallel to the applied bias field direction. There are a few more per million parallel than antiparallel so that all of the nuclear magnetic moments at equilibrium sum to a small magnetic moment aligned parallel to the bias field. When pulses of radiofrequency energy are fed into the system at energy levels above saturation, all of the nuclei will precess or rotate around the direction of the applied radiofrequency magnetic field. That means that the resultant magnetic moment also rotates around the applied radiofrequency field. The rate of rotation in radians per second is directly proportional to the strength of the radiofrequency field. By controlling the length of time the radiofrequency pulse is applied, the angle through which the resultant magnetic moment is rotated can be controlled. If one stops at  $90^\circ$ ,  $180^\circ$  or  $270^\circ$ , the nuclei or free electrons are out of equilibrium with their surroundings and they lose energy to their surroundings at the  $T_1$  rate, so that in a time equal to  $5T_1$ , almost all of these pulse-rotated magnetic moments have returned to equilibrium which is alignment with the bias field from which they can be rotated again.

When the nuclei are rotated  $90^\circ$  and the radiofrequency pulse is removed, in addition to the exponential return-to-equilibrium at the  $T_1$  rate, there is also a dispersion of the magnetic moment vectors at a rate of  $T_2$ . As was described before, at equilibrium, there are more magnetic moments aligned parallel to the field than antiparallel to the field, giving the net nuclear magnetic moment which is rotated by the radiofrequency pulse. When the net nuclear magnetic moment is a  $90^\circ$  and free of the radiofrequency pulse, it then precesses around the direction of the bias field at a rate dependent upon the intensity of the magnetic field. Each nuclear moment is going to have a different magnetic field at its position because of inhomogeneities in the bias magnetic field over the finite sample volume and because of internal magnetic fields from neighboring nuclei with magnetic moments. The magnetic moment vectors, for each nucleus or for a small group of nuclei, can now be considered to precess at different rates because they are in different magnetic fields and the pre-

cession rate is directly proportional to the bias field. Therefore, they tend to disperse and fan out rather than continue to act as a single net vector. Thus, the vector summation of these magnetic moments starts out at the net value at the end of the  $90^\circ$  pulse and then decreases exponentially, at a rate of  $T_2$ , until at a time equal to  $5T_2$ , the nuclear magnetization is zero in the plane perpendicular to the direction of the applied bias field.

As described above, there are two decay rates or relaxation times associated with the transient nuclear magnetic resonance technique,  $T_1$  and  $T_2$ . The value of  $T_1$  describes the thermal coupling between the resonating nuclei and their surroundings sometimes called the lattice. The better the coupling, the shorter the value of  $T_1$ . The value of  $T_2$  describes the inhomogeneity of the bias magnet, and the magnetic influence between neighboring resonating nuclei.  $T_2$  is always smaller than  $T_1$ . From the values of  $T_1$  and  $T_2$ , the Debye relaxation time can be calculated. Thus, from a knowledge of  $T_1$  and  $T_2$ , information relating to the surroundings of the resonating nuclei can be obtained.

Two types of transient NMR signals are usually used: (1) a free induction decay following a  $90^\circ$  pulse, and (2) an echo following dual pulse sequences such as: (a) two  $90^\circ$  pulses, (b) a  $90^\circ$  pulse followed at a time  $T_1$  by a  $180^\circ$  pulse, or (c) a  $180^\circ$  pulse followed at a time  $T_1$  by a  $90^\circ$  pulse. The transient NMR signals following a single  $90^\circ$  pulse and a dual  $90^\circ$ - $180^\circ$  pulse sequence are given in Figures 1a and 1b. The NMR signal in Figure 1a is called the free induction decay or FID. The NMR signal in Figure 1b is called the spin echo.

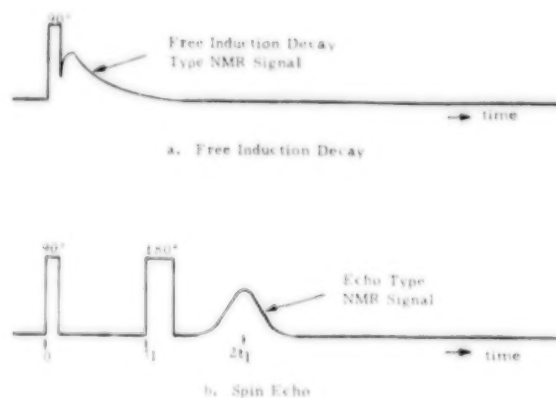


Figure 1. Two types of transient NMR signals. a. Free induction decay following a single  $90^\circ$  pulse b. Spin echo following a dual  $90^\circ$ - $180^\circ$  pulse sequence.



With either method, steady-state or transient, signals can be obtained which are proportional to the number of nuclei or free electrons in the volume being sampled. This gives quantitative analyses. The phenomenon occurs at a ratio of frequency to magnetic bias field intensity which is different for the nuclei of each isotope with a nuclear magnetic moment and for free electrons. For example, the magnetic resonance phenomenon for hydrogen nuclei occurs at 4257.6 Hz per Gauss. For free electrons, resonance usually occurs at  $2.8 \times 10^6$  Hz per Gauss. Specific frequencies for the nuclei of specific isotopes can give quantitative analyses for isotopes and elements.

Using the transient mode of operation with the hydrogen nuclei and the steady-state mode for free electrons, many measurements on explosives and propellants have been made. The results of these measurements are given in the following section.

#### IV. NUCLEAR MAGNETIC RESONANCE SIGNALS IN MATERIALS

Because there is more restriction to molecular motion in solids than in liquids, the value of  $T_2$  for the hydrogen transient NMR signal from a liquid should be greater than the  $T_2$  from a solid. Thus, in a mixture composed of a liquid and solid, the hydrogen transient NMR signal will have two components: one with a short  $T_2$  from the hydrogen in the solid and one with a longer  $T_2$  from the hydrogen in the liquid. If the liquid is absorbed or adsorbed by the solid, then the  $T_2$  of the absorbed or adsorbed liquid will be shorter than if the liquid were free. An example of a mixture with no liquid absorption is sand and water. An example of a mixture with liquid absorption is starch and water. There is no perceptible change in the  $T_2$  of the water when a small amount of sand is added. The change in  $T_2$  is small even when the weight of the sand may be ten times the weight of the water. However, there is a large change in the  $T_2$  of the water when a small amount of starch is added. The difference is that starch is a material which absorbs or adsorbs the water and thus increases its effective viscosity or lowers the relative motion of neighboring hydrogen nuclei and thereby reduces the value of  $T_2$ . Therefore, the value of  $T_2$  decreases linearly with increasing viscosity when plotted on a log-log scale.

The explosives and propellants of interest will contain solids and liquids. In some of the mixtures, the only liquid will be water. In other mix-

tures, there are liquids which are one or more of the desired components. The hydrogen transient NMR signal from these materials can be used to measure moisture if the signal component from the hydrogen in the water is separated from the signals from the hydrogen in the remainder of the components. This can be readily accomplished if the  $T_2$  values for all of the components are quite different. The closer they are to each other, the more difficult is the separation. The signal separation problems can best be demonstrated by the signals from some of the explosive and propellant materials of interest. The signals used will be from black powder, M-10 type propellant, T-36 type propellant, RDX, TNT, Composition B, and Type C-4 plastic explosive using RDX.

##### A. Signals from Black Powder

A representative hydrogen transient NMR free induction decay type signal from black powder is given in Figure 2. The black powder should have hydrogen in only the water, but it was found that there was a residue of incompletely pyrolyzed hydrocarbon or hydrogen-containing material remaining in the charcoal. Therefore, in Figure 2 there are two hydrogen decay curves comprising the hydrogen free induction decay signal from the hydrogen in black powder. The one with the fastest decay rate comes from the hydrogen in the incompletely pyrolyzed material in the charcoal and that component is labeled "solid" in Figure 2 since that signal came from the hydrogen in the solid part of the black powder. The second component in Figure 2 has a much smaller amplitude and a much longer decay rate and it comes from the hydrogen in the water or the liquid part of the black powder. Since these signals are exponential type decay signals, a measurement at any time on their decay can be used to give the initial value at time equal to zero if the decay rate is known. Fortunately, the decay rates for the solid and liquid components were known and were functions of only the temperature. Therefore, the signal proportional to the total hydrogen in the black powder sample could be determined by measuring the amplitude of the signal in Figure 2 at time "A" between 12 and 15 microseconds. The liquid component amplitude will need to be measured when the solid component has decayed to essentially zero. This occurs at time "B" in Figure 2 between 55 and 65 microseconds. Now we have two signals, one proportional to the total hydrogen in the solid plus the liquid at around 13.5 microseconds and a second proportional to the liquid



signal at around 60 microseconds. To compare the two amplitudes, the liquid at 13.5 microseconds must be calculated. Since the decay time is known, this means nothing more than multiplying the value at 60 microseconds by the value to bring the time to 13.5 microseconds. When this is done, then values can be used to find the percent moisture on either a dry or wet basis.

### B. Signals from Type M-10 Propellant

The hydrogen transient NMR signal from Type M-10 propellant is given in Figure 3. The solid signal component has a different shape from the solid signal component in black powder. However, changed the shape, the solid plus liquid value amplitude can be measured at time "A" or between 12 and 15 microseconds while the liquid component can be determined at time "B" between 55 and 65 microseconds. This is possible because, even though the shape of the solid signal changed, it had still decayed to an insignificant value by 60 microseconds.

To further investigate this possibility, a signal was recorded with the oscilloscope amplification 10 times higher. The signal shown in Figure 4 was obtained. The solid plus liquid component was

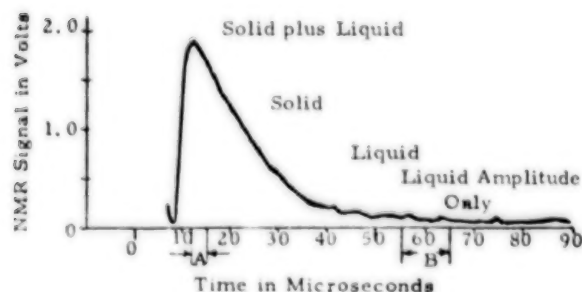


Figure 2. Free induction decay type hydrogen transient NMR signal from black powder at 30 MHz.

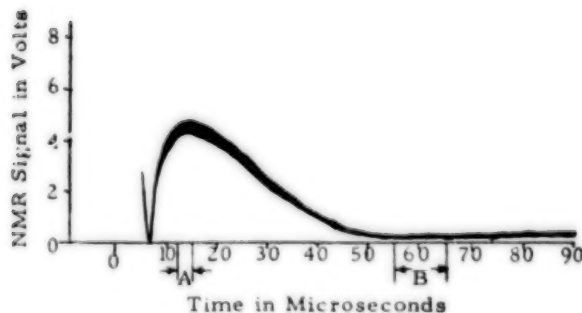


Figure 3. Free induction decay type hydrogen transient NMR signal from M-10 material at 30 MHz.

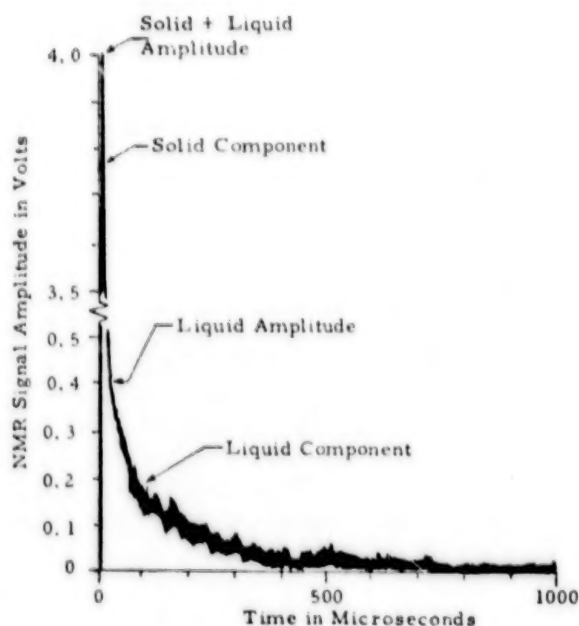


Figure 4. Free induction hydrogen NMR signal from M-10 type material at 30 MHz.

added graphically to keep the perspective. The liquid decay has only one component since it has only one exponential in the decay curve. Therefore, the measurement of moisture in Type M-10 propellant can be accomplished with the same simple procedure as was used with black powder.

### c. Signals from Type T-36 Propellant

The normally observed hydrogen transient NMR signal from Type T-36 material is given in Figure 5. When the amplification of the oscilloscope is doubled, and the time scale is lengthened by 20 times, the signal from T-36 appears as shown in Figure 6. The T-36 material contains two liquids, ethyl centralite and water. The liquid amplitude at 60 microseconds contains components from the decays from both liquids. To separate the two components, the voltage proportional to the hydrogen in the liquid with the longest decay rate should be measured at a time when the component from the other liquid has decayed to an insignificant value. It is most probable that the component with the longest decay rate is ethyl centralite, at a concentration of 1.5%. It is most probable that its concentration can be measured at around 200 microseconds, at which time the moisture signal component should have decayed to insignificance. The three measurements at the three different times (13.5 microseconds, 60 microseconds, and 200 microseconds) can be used to deter-

mine the percent moisture again without weighing the sample: at 13.5 microseconds, solid plus both liquids; at 60 microseconds, both liquids; at 200 microseconds, the second liquid. The second liquid subtracted from both liquids give the first liquid. When both are divided by the value at 13.5 microseconds, the hydrogen ratios are obtained. The hydrogen ratios are converted into moisture percentages on a weight basis through the use of the proper conversion factors.

#### D. Signals from RDX Type Explosive

The free induction decay type signal from RDX is given in Figure 7. The signal component from the hydrogen in the solid RDX is labeled in Figure 7. There appear to be two other signals between 20 and 50 microseconds and 70 and 90 microseconds. These are not signals from another source but are due to Lowe-Norberg or "solid" beats from the hydrogen in the solid RDX. The water content of the sample used for Figure 7 was below 0.25% but it was never measured with the usual oven or titration techniques because only one sample was available and it had to be preserved. It would appear, however, that moisture measurements in RDX would be much like the measurements with M-10 and black powder. The two measurements would be made at 13.5 and 60 microseconds. The moisture value would be calculated through the use of the appropriate conversion constants.

#### E. Signals from TNT Explosives

##### 1. Signals from Solid TNT

The free induction decay type hydrogen transient NMR signal from the TNT type explosive is given in Figure 8. When the NMR signal from TNT in Figure 8 is compared with the NMR signal from RDX in Figure 7, it can be concluded first that the decay rate for TNT is slower than the decay rate for RDX. The longer decay rate means

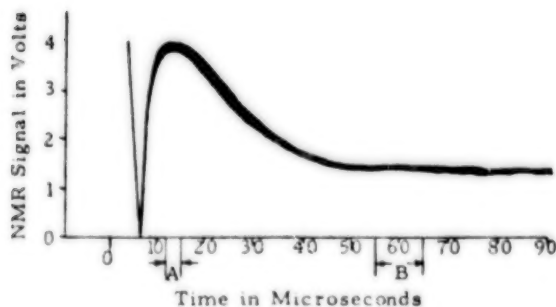


Figure 5. Free induction decay type hydrogen transient NMR signal from T-36 material at 30 MHz.

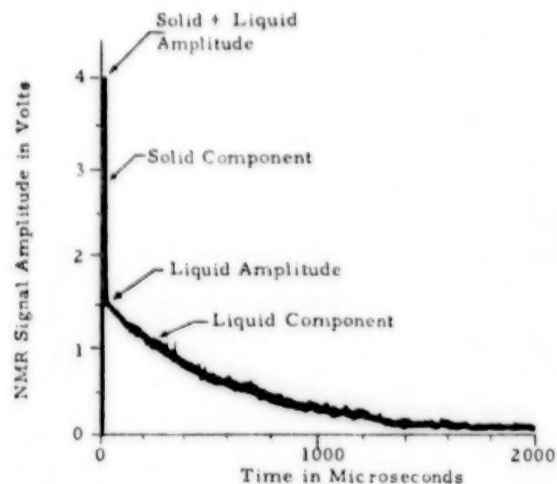


Figure 6. Free induction hydrogen NMR signal from T-36 type materials at 30 MHz.

that the signal from the water must be taken at a time later than 100 microseconds.

It can be concluded secondly from the above comparison, that the total signal, solid plus liquid, should be measured slightly later for TNT than for RDX, or between 15 and 18 microseconds.

Here again, as for other materials, the percentage moisture can be determined from two meas-

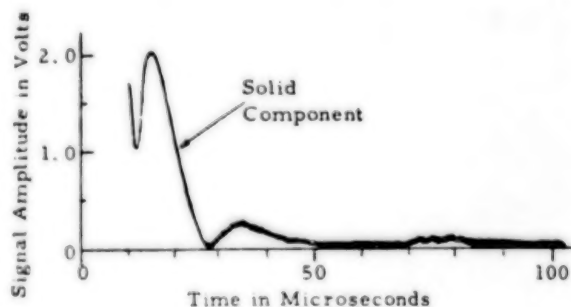


Figure 7. Free induction decay type hydrogen transient NMR signal from RDX at 2.5 MHz.

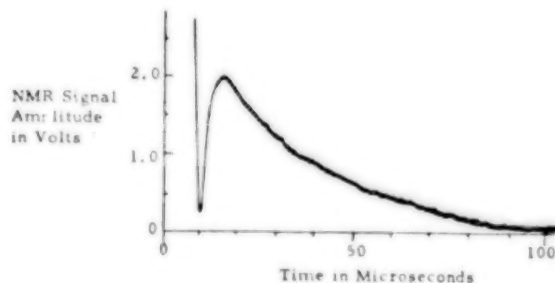


Figure 8. Graph of the free induction decay type of hydrogen transient NMR signal from TNT.

measurements of the amplitude of the signal from TNT in Figure 8. One measurement should be centered at 16.5 microseconds for the solid plus liquid (water) value and one at 110 microseconds for the liquid (water) value. These two values can then be used as previously presented to calculate the percentage moisture once the conversion factor has been determined from hydrogen transient NMR measurements on many samples of TNT having moisture values spread over the expected range.

## 2. Signals from Melted TNT

Using a small sample available at SwRI, nuclear magnetic resonance measurements were made on melted TNT. The sample of TNT was melted in boiling water and inserted into the laboratory type transient NMR system at SwRI. Sequential photographs of the transient NMR signals were made as the TNT solidified. The results are reproduced in Figure 9. No attempt was made to measure the temperature of the TNT as it cooled undisturbed in the apparatus. The transient NMR signals observed and pictured are the free induction decay responses described previously. In this laboratory NMR system, the magnet inhomogeneity effect is smaller than the  $T_2$  of the material and the signals display the true spin-spin relaxation times,  $T_2$ , of the solid and liquid components of the TNT as it changes from the melted to the solid condition.

The free induction decay response in Figure 9a is for the TNT just after melting. By measuring and comparing the amplitudes of the response at appropriate points (illustrated by A and B in Figure 9a), it may be seen that the percent liquids at this time is  $(3.6/4) 100$  or 90 percent. After 15 minutes, the percent liquid is  $(1.5/4) 100$  or 37.5%. After 20 minutes, the percent liquid has dropped to  $(0.6/4) 100$  or 15%. After 23 minutes, the percent liquid is  $(0.1/4) 100$  or 2.5%; see Figures 9b, 9c, and 9d.

In Figure 9, as the amount of liquid decreased, the total signal, the solid plus liquid, or the amplitude of the sharply peaked signal between zero and 0.2 milliseconds, did not change in amplitude but stayed fixed at 4 volts. This means that the transient NMR "sees" the total hydrogen in the sample, solid plus liquid. It also separately "sees" the hydrogen in the liquid. The graphs in Figure 9 also show that the amount of solid is obtained simply by subtracting the voltage proportional to the hydrogen in the liquid TNT from the voltage proportional to the total hydrogen in the sample solid plus liquid. To obtain the total hydrogen (solid plus liquid) from an NMR response like

those in Figure 9, the signal amplitude would be sampled as quickly as possible (10 to 20 microseconds) after the end of the  $90^\circ$  radiofrequency pulse. For the liquid component, the signal amplitude would be sampled as quickly as possible after the solid signal component has decayed to near zero level. As may be seen in the examples, the optimum time for sampling the liquid component is on the order of 0.2 milliseconds after the start of the  $90^\circ$  pulse.

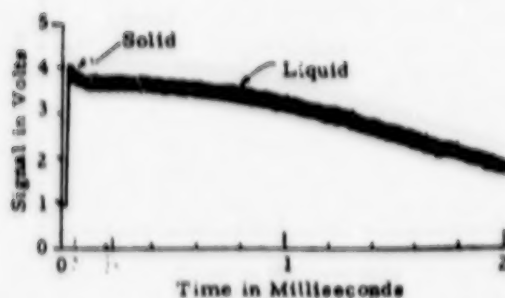
## F. Signals from Composition B Explosive

Composition B is a mixture of 60% RDX, 39% TNT and 1% wax for a desensitizer. The free induction decay type of hydrogen transient NMR signal from Composition B is given in Figure 10. It appears to be a combination of Figures 8 and 9 in that there appear to be two components; one with a rapid decay like RDX and one with a longer decay like TNT. The signal from the wax and the water do not stand out in the signal in Figure 10. Therefore, in order to determine where in time to make the amplitude measurements on the TNT free induction decay signal to enable the calculation of the moisture percentage without weighing the sample, many NMR measurements will need to be made on many samples with moisture values spread over the range of interest. From these many measurements can be obtained the conversion constants to convert the voltage ratios to percent moisture.

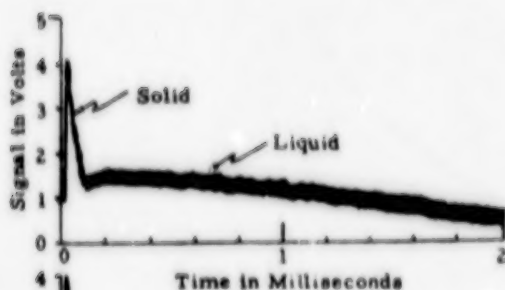
## G. Signals from Type C-4 Plastic Explosive

The free induction decay type of hydrogen transient NMR signals from RDX base Type C-4 plastic explosive is given in Figure 11 on the same time scale (100 microseconds) as most of the other signals previously presented. Type C-4 explosive has both solid and liquid components as shown in Figure 10. The measurement signals in Figure 10 were made at 2.5 MHz while the signals from the other explosives, except for RDX, were made at 30 MHz. Therefore, there is more noise on the signal from C-4 than from the other explosives at 30 MHz. The signal from C-4 has more noise than the RDX at the same frequency because the sample of C-4 was smaller than the sample of RDX.

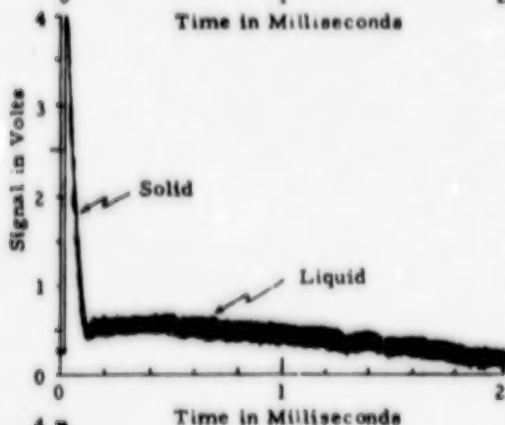
Type C-4 is composed of 91% RDX, 2.1% polyisobutylene, 1.6% motor oil, and 5.3% di(2-ethylhexyl) sebacate. There are thus more liquids than the one, water, an impurity, to be measured. All of the liquid signal, not just the first 100 microseconds, is displayed in Figure 12. An experienced observer of free induction decay signals



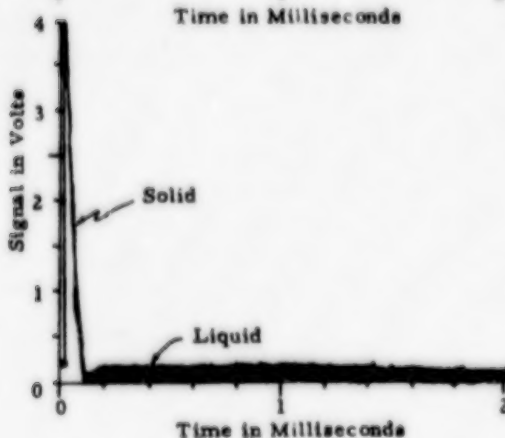
- a. TNT Just After Melting  
 Solid Plus Liquid = 4  
 Liquid = 3.6  
 Solid = 0.4



- b. TNT After Cooling 15 Minutes  
 Solid Plus Liquid = 4  
 Liquid = 1.5  
 Solid = 2.5



- c. TNT After Cooling 20 Minutes  
 Solid Plus Liquid = 4  
 Liquid = 0.6  
 Solid = 3.4



- d. TNT After Cooling 23 Minutes  
 Solid Plus Liquid = 4  
 Liquid = 0.1  
 Solid = 3.9

Figure 9. Free induction decay NMR signals from melted TNT as it cooled and solidified.

would conclude that there are two or more exponential decays comprising the liquid decay signal, since it is a straight line for more than 3000 microseconds (3 milliseconds).

In order to use NMR to measure the amount of

moisture in Type C-4 explosive, the measurement times and conversion factors must be determined by performing NMR measurements on a significant number of samples of C-4 having moisture values over the range expected, or from 0.1% to 1%.



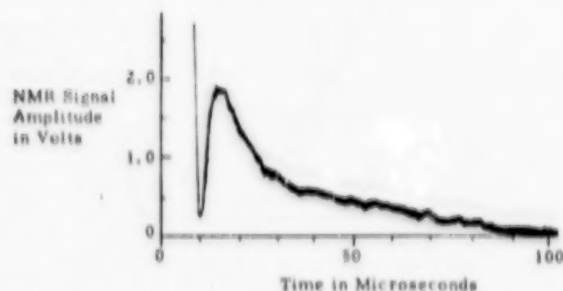


Figure 10. Graph of the free induction decay type of hydrogen transient NMR signal from Composition B.

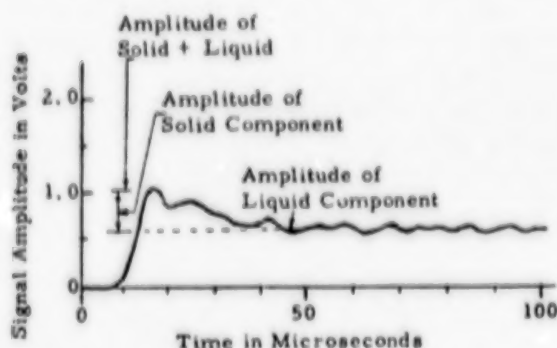


Figure 11. First 100 microseconds of the free induction decay type hydrogen transient NMR signal from C-4 (RDX Base) at 2.5 MHz.

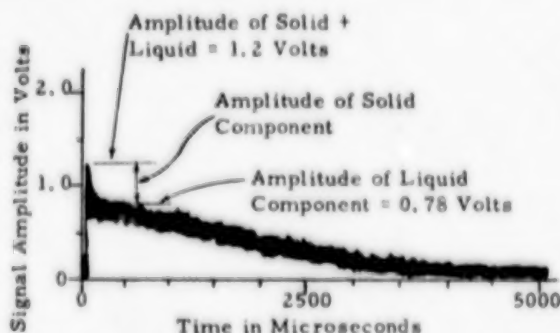


Figure 12. All of the free induction decay type of hydrogen type transient NMR signal from C-4 (RDX Base) at a 2.5 MHz.

#### H. Summary from NMR Signals in Explosives

The materials of interest are RDX, TNT, Composition B, M-55 detonator mixture, C-4, A-2, A-3, A-4, black powder, T-36 and M-10. Hydrogen transient NMR signals have been shown for all of the above materials except the M-55 detonator mixture, A-2, A-3 and A-4. All of the data presented indicates that the hydrogen transient NMR signals can be used to determine the moisture content, on a weight percent basis, when the

proper positions in time are found to take the data and when the proper conversion constants are used to convert voltage ratios to weight percent concentrations.

Hydrogen transient NMR signals from the M-55 detonator mixture and the three type-A compositions were not presented because samples have not been available in previous projects. However, the compositions of these materials are not significantly different from the compositions of the materials whose hydrogen transient NMR signals have been presented. That is, the hydrogen transient NMR signals from compositions A-2, A-3, and A-4 should be similar to the signals from Composition B since the type-A compositions are mixtures of more than 90% RDX and densitizing wax which have been pressed at 3000 to 12,000 psi. Therefore, the type-A compositions contain essentially two solid components with only one liquid component, water.

In the M-55 detonator mixture, all of the components of the mixture are solids and any liquid present should be water. Therefore, the hydrogen transient NMR signal from the M-55 detonator mixture should not be much different from the signal presented from M-10. If this assumption holds true, then moisture measurements in M-55 detonator mixtures could be made by sampling the signal voltage at two times similar to the procedure described for M-10. Of course, the two measurement-time values may be different from the M-55 detonator mixture and different conversion constants may need to be used. The values of measurement times and conversion constants will need to be determined from hydrogen transient NMR measurements on samples of M-55 detonator mixture with known values of moisture over the range of interest.

#### V. ELECTRON MAGNETIC RESONANCE SIGNALS IN MATERIALS

Several types of explosives and propellants were scanned with an electron magnetic resonance spectrometer operating at approximately 9,600 MHz in a magnetic field of 3400 Gauss. No free electron signal was obtained from RDX, TNT, Composition B, or Composition C-4.

A very strong free electron signal was obtained from black powder as demonstrated by the recorded signal given in Figure 13a. A much weaker free electron signal was obtained from smokeless powder as shown by the signal in Figure 13b. The smaller signal from smokeless powder is caused by

the much lower concentration of charcoal in smokeless powder where it is used only as a glaze on each grain. If the same amount of black powder and smokeless powder is used, the free electron signal from the black powder is about 250 times that from the smokeless powder.

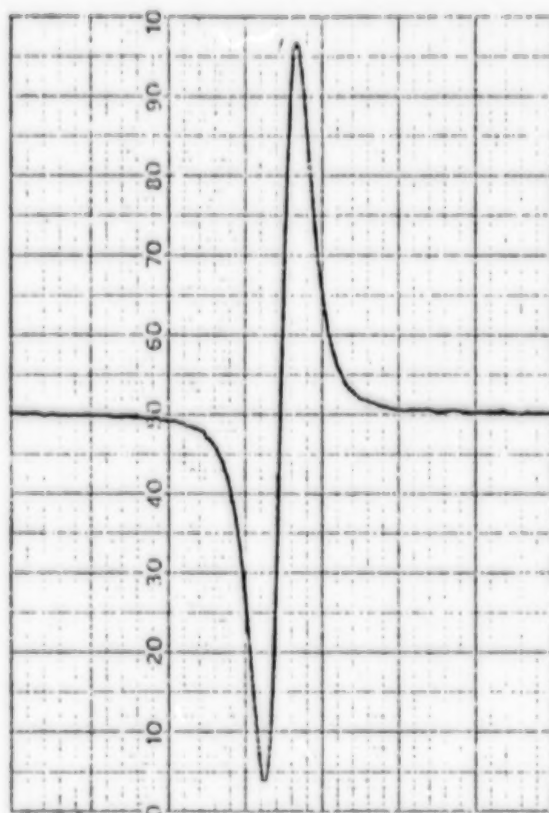
The free electrons in the charcoal are caused by the pyrolysis. Broken bonds are caused in the large hydrocarbon molecules which result in an electron being set free. This free electron will be trapped in a potential energy well somewhere in the material where it will remain. Since the energy needed to bring the free electron out of the well is larger than its thermal energy, the free electron remains in the well and can be detected by the electron magnetic resonance spectrometer. If the charcoal were heated at a temperature higher than that necessary to bring the free electron out of its well, it could be

lost by pairing with another and reduce the free electron magnetic resonance signal.

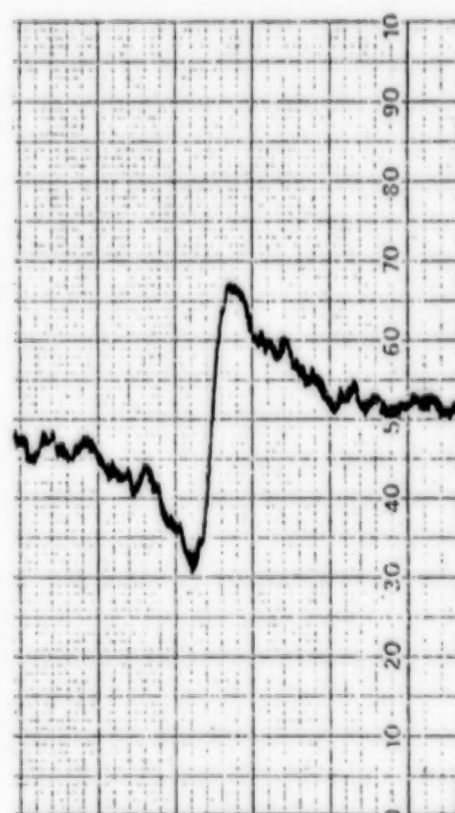
## VI. SPECIALIZED NMR AND EMR INSTRUMENTATION

### A. Background

Work with NMR and EMR by most investigators in the past has usually been laboratory studies with small samples and large, delicate apparatus. The sample to be studied is placed in the detection coil located in a large magnet, and by careful adjustment and utilization of the system, excellent NMR data can be obtained. Data are most commonly presented in graphical form. Typical laboratory NMR instrumentation will accommodate samples with a maximum diameter of a centimeter or two and a maximum length of two or three cen-



a. Black Powder (Dupont FF<sub>g</sub> Superfine Black Rifle Powder)  
Quantity: 1 Flake  
Gain: X10  
Frequency:  $\approx 10$  GHz



b. Smokeless Powder (Dupont IMR-3031)  
Quantity: 10 grains  
Gain: X100  
Frequency:  $\approx 10$  GHz

Figure 13. ESR response of black and smokeless powder.



timeters. In many cases, where high resolution measurements are required, the maximum allowable sample size is even smaller. Common laboratory type EMR equipment imposes even more stringent limitations on sample size and shape. Again, the equipment is quite large compared to the allowable sample size, requires critical adjustment, and is also quite delicate. By careful adjustment of the instrument, however, excellent results can usually be obtained in a graphical form. These laboratory type magnetic resonance instruments are excellent for the study of the characteristics of those materials where a representative sample is available in a sufficiently small size. A selection of instruments of these types are available and routinely used at Southwest Research Institute. These laboratory instruments are suited for laboratory studies of the chemical characteristics but would not be suited for use in field, industrial, or critical environments. On the basis of the prior experience gained at SwRI in the design and fabrication of advanced NMR and EMR systems, however, the development of specialized systems that would be entirely suitable is considered to be both feasible and practical.

Development of advanced NMR and EMR instrumentation systems to meet the special requirements of a variety of difficult measurement, detection, and control applications has been a major activity at Southwest Research Institute for the past 28 years. A number of NMR instruments have been developed for accurate quantitative measurements of particular constituents, such as moisture, in a variety of products and base materials. Systems which will accommodate samples up to  $14 \times 23$  inches in cross-section, which have effective sample volumes of up to 5,000 cubic inches, and which are suitable for the detection and measurement of the NMR response from solid as well as liquid materials have also been developed. Other NMR systems have been developed for measurements on samples located outside the physical extent of the apparatus, such as is required, for example, for sensing buried materials. In addition, unique discriminating techniques have been developed to permit the use of NMR to detect small quantities of particular compounds of interest even in the presence of large quantities of background materials containing similar nuclei. These efforts have helped advance NMR from the status of a laboratory research and analytical tool to that of a practical measurement technique for a wide range of industrial, commercial, environ-

mental, security and military applications.

A number of specialized EMR systems have also been developed at SwRI and further efforts in this area are currently underway. This work has included the development of relatively low frequency EMR systems which will accommodate large samples (several liters) and provide the very high sensitivity required for research purposes. Special detection methods have been developed to overcome the critical adjustment requirements of laboratory EMR systems and to allow practical detection of the response from unstable, discontinuous, and moving samples. Other systems have been developed for detection and measurement of the EMR response of charcoal and charcoal-based materials passing through an open aperture approximately 0.5 meter wide and 0.4 meter high. A part of the current work is directed toward development of an EMR system for continuous, *in situ* measurement of the thickness of the layer of coal remaining over the substrate (shale or sandstone) during mining operations.

The experience gained at SwRI in the previous programs has resulted in the basic science and technology, the creative staff and the facilities required to efficiently and successfully apply the NMR and EMR techniques to unique situations. On the basis of this background, SwRI is well equipped to conduct the research studies and to develop the specialized instrumentation that are required to successfully apply the NMR and EMR methods to the material measurements of interest.

## B. NMR Equipment Possibilities

The block diagram in Figure 14 gives the basic components needed to obtain a transient NMR signal, process it according to some requirement

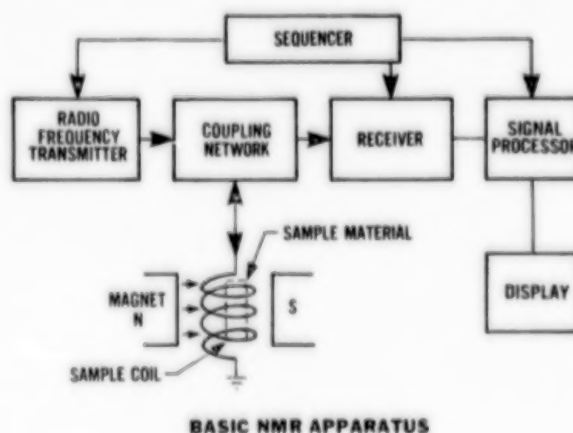


Figure 14. Block diagram of typical transient NMR system.

and display the processed data. Any magnetic resonance device for hydrogen in explosives or propellants would have the same basic block diagram. The sequencer, since this is a transient system, controls the timing of the radiofrequency pulses out of the transmitter, the gating of the receiver and the sampling of the signal amplitudes in the signal processor. The signal processor can then either display the signal amplitudes at two or three different times or it can process these two or three values to give the percentage amounts of each component containing hydrogen in the explosive or propellant.

The detection head, composed of the detection coil or sample coil and the magnet in Figure 15, may be different in shape and size depending upon where it is to be used. For example, if the measurement of hydrogen in explosives or propellant is to be made on a flowing process stream, the detection head shown in Figure 15 can be used. As the material flows through the sampled volume in the RF coil, the signal is taken from that section of the sample inside of the RF coil. The section of the process pipe inside the radiofrequency coil must be constructed from nonconducting materials having a low dielectric constant.

The same shape and size of detection head as described above can also be used for nonflowing or stationary samples in test tubes or other containers which will fit inside of the hole through the radiofrequency coil.

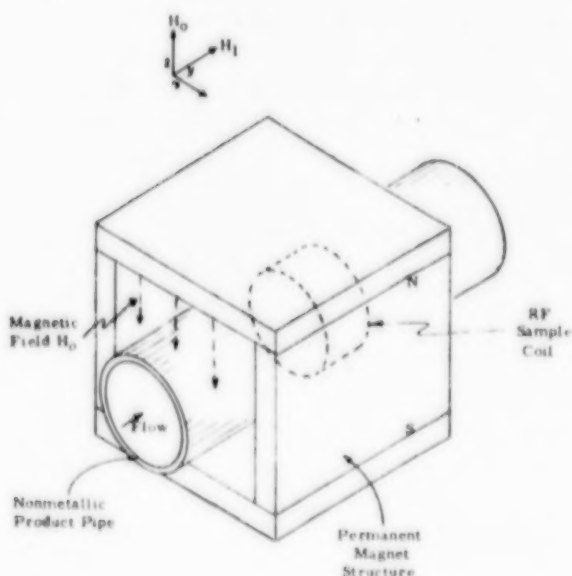


Figure 15. Sketch illustrating the sensing head concept for the magnetic resonance instrumentation.

However, other measurement potentials exist if the detection head is made as drawn in Figure 16. When the magnet has a U-shape and the coil is a very short solenoid or a flat spiral, it is possible to make the conditions for the observance of the nuclear magnetic resonance absorption at a distance from the magnet. The conditions required are:

(a) The frequency,  $f_0$ , of the radiofrequency field,  $H_1$ , and the intensity of the magnet field,  $H_0$ , obey the relationship  $2 f_0 = \gamma H_0$ , where  $\gamma$  is the gyromagnetic ratio which for hydrogen is 26,751.29 radians per second per Gauss. For free electrons,  $\gamma$  is  $17.6 \times 10^6$  radians per second per Gauss.

(b) The radiofrequency field,  $H_1$ , be at right angles to the direction of the magnetic field,  $H_0$ , as shown in Figure 16.

(c) The radiofrequency field,  $H_1$ , be of the proper intensity to cause the nuclei to be rotated through the angle desired,  $90^\circ$ ,  $180^\circ$ , or whatever angle is chosen. If the steady-state is used, then  $H_1$  will be less than that needed for saturation.

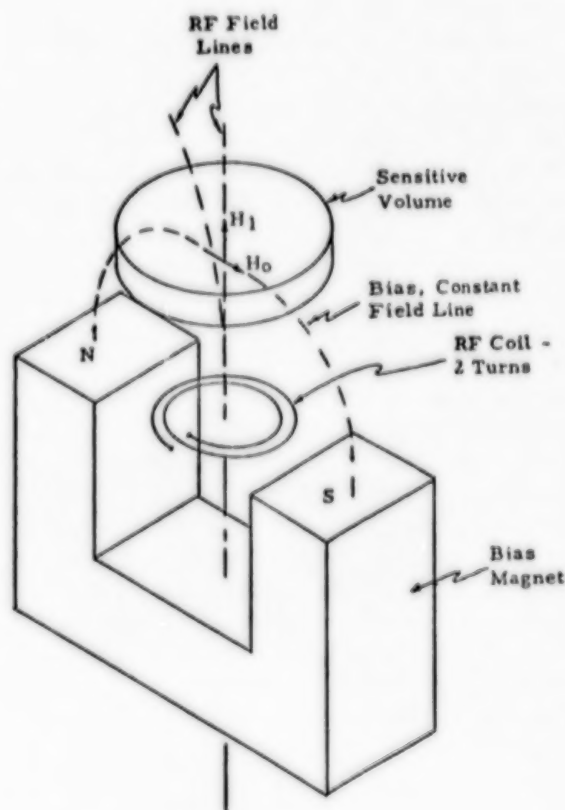


Figure 16. Manifestation of the NMR detection head where the sensitive volume is outside of the magnet and RF coil configuration.

All of these conditions can be met in a specific volume at a specific distance from the detection head. Through the use of another magnet, smaller or larger than the U-shaped magnet in Figure 16, the field can be made relatively homogeneous over a small volume spaced a short distance of from  $\frac{1}{2}$  in. to 1 in. from the detection head. At the signal levels experienced from the EMR signals from black powder, a magnetic field of 100 Gauss (280 MHz) should be sufficient for such EMR signals. Such a field is readily obtained at 1 in. from the magnet. For hydrogen nuclei in explosives and propellants, fields of 700 to 1000 Gauss are needed at distances of from  $\frac{1}{2}$  in. to 4 in. Therefore, hydrogen and free electron signals could be obtained from explosives and propellants at distances of from  $\frac{1}{2}$  in. to 4 in. away from the magnet-detection-coil system shown in Figure 16. To detect hydrogen in moisture in concentrations of from 0.1 to 1.0 percent, magnetic field values of 7000 Gauss are needed.

The same detection head could detect the hydrogen transient NMR signals from explosives and propellants as they are carried on an endless belt

system. Such belts are usually in a shallow V-shape and the detection head could be mounted underneath the belt so as to detect the resonance of the hydrogen nuclei, not in the belt, but above the belt in the explosive or propellant carried on the belt from  $\frac{1}{2}$  in. to 1 in. away from the detection head.

Such detection heads could be mounted on a thin plastic section inserted in the wall of a large product pipe if it was inconvenient to use a thief tube run through the detection head configuration in Figure 15. Here again, hydrogen nuclei or free electrons would be detected at distances of from  $\frac{1}{2}$  in. to 4 in. away from the detection head into the product being carried through the pipe.

Other detection head configurations are possible, and this description is not meant to be an exhaustive study of the possibilities. It does, however, indicate some of the most obvious applications of the two basic detection head configurations given in Figures 15 and 16. To the present, detection volumes 14 inches high, 24 inches wide and 30 inches deep have been accommodated in the magnet style in Figure 15.



## **EXPLOSIVE DETECTION**

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## **EXPLOSIVES DETECTION PROGRAM AT SANDIA NATIONAL LABORATORIES**

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**ABSTRACT.** A brief, general description of the Explosives Detection Program at Sandia National Laboratories is given. The six major topics of the program are: (1) Coated or Uncoated Metallic Preconcentrators; (2) a Derivatization Study; (3) a Portable Ion Mobility Spectrometer; (4) an Explosives Screening Portal; (5) Mass Spectrometer Development; and (6) an Explosive Vapor Generator.

### **INTRODUCTION**

Many organizations throughout the world are interested in developing an effective explosives detector; Sandia National Laboratories under the Department of Energy (DOE) is no exception. All organizations have requirements unique to their particular interest in the study of explosives detection. Sandia is working on a program investigating vapor detection techniques for the sensing of explosives materials. This paper presents a brief, general description of that program.

The six major topics of the program are: (1) Coated or Uncoated Metallic Preconcentrators; (2) a Derivatization Study; (3) a Portable Ion Mobility Spectrometer; (4) an Explosives Screening Portal; (5) Mass Spectrometer Development; and (6) an Explosive Vapor Generator.

### **COATED OR UNCOATED METALLIC PRECONCENTRATORS**

A study was undertaken with the Department of Chemistry at the University of Texas (UT) at Austin. The purpose of the study was a better understanding of preconcentration on metallic substrates. Hopefully, the study will determine how explosives molecules are picked up, how they are held, how they are released when heated, and the temperature of release.

In the initial experiment, a single crystal of platinum was dosed with TNT molecules. This was followed by Thermal Desorption Spectroscopy (TDS) of the molecules. Auger Electron

Spectroscopy indicated that the surface of the platinum crystal was coated with carbon after the TDS.

The researchers at UT found that the evolution of the explosive molecules from this preconcentrator occurs at temperatures much lower than expected. When TNT is adsorbed at 100 K, there are two peaks in the desorption spectra. The first peak occurs below room temperature at 262-270 K and the second peak occurs just above room temperature at 300-330 K. When studies were conducted at room temperature, the one remaining peak desorbed at the higher temperature and showed approximately the same characteristics as in the lower temperature work. This information indicated that metallic preconcentrators are much more efficient in environments cooler than room temperature.

### **DERIVATIZATION STUDY**

Because explosives have low vapor pressures, they provide relatively few molecules with which to work. In addition, the tendency for explosives molecules to adsorb on surfaces makes it difficult to flow them through a tube to a detector. However, forming a derivative of the molecules may make it easier to work with them. A study is underway to investigate this concept. It has been determined that a gas-phase reaction will probably be impossible; however, it is remotely possible that one could form a derivative while the molecules are in contact with a metallic surface.

## PORTABLE ION MOBILITY SPECTROMETER (IMS)

The IMS unit is one of the most sensitive devices for detecting TNT and DNT. Its ultimate sensitivity for TNT is in the range of one part per trillion. The commercial IMS is a large laboratory instrument that requires a supply of zero air for the drift flow. PCP, Incorporated, has manufactured a more portable IMS with a special air purification system which obviates the need for gas bottles. The total flow of the gas enters the inlet. A part of the exit flow is passed through the purification system and then is reused as the drift gas. We find that the sensitivity of this "more portable" ion mobility spectrometer is equivalent to the laboratory model and although it is still rather large, it is at least possible to place it in a 24 inch  $\times$  24 inch  $\times$  36 inch cart for transportation. Currently, small and more rugged IMS models are being investigated.

## EXPLOSIVES SCREENING PORTAL

A "Request for Quote" was sent to all known producers of commercial explosives detectors asking them to submit portal configuration designs using their explosives detectors. A contract was placed with Xon-Tech, Incorporated, to build an explosives screening portal. In addition, a unit has been purchased from Ion Track Instruments, a division of Analytical Instruments of England. A Sentex Portal has also been purchased. Comparative testing of these units using many different explosives is now being conducted.

One of the problems in portal explosive detection is that there are too few molecules to detect easily. When these molecules are further diluted by the air flow in the portal they can only be detected by an extremely sensitive detector. At the present time, commercial detectors have no problem in detecting bomb quantities of dynamite; however, with this new series of portals, it is hoped the range of detection can be extended to include military grade TNT. If the range of detection is extended to include most of the TNT samples, then only two major explosives of interest, RDX and PETN, will remain to be detected.

## MASS SPECTROMETER DEVELOPMENT

When scientists are asked what kind of instrument they would use for detecting extremely small amounts of explosives vapors, almost invariably

they mention a mass spectrometer. Those who have worked with the different applications of mass spectrometers will acknowledge that one of the major problems is finding an ion source that will not fracture these fragile molecules. The mass spectrometer has the sensitivity to detect a very small number of molecules; however, if the molecules are not transported into the mass spectrometer and ionized without degradation, there is no sensitivity. Negative ion formation is a possible means of ionization with low fragmentation. Since explosives molecules are highly electronegative, it should be possible, with low energy electrons, to form  $M^-$  ions of these molecules by resonance capture. Negative ionization should be desirable for at least two reasons: (1) most of the organic compounds in nature do not form negative ions, and (2) most of the explosives molecules should be in the  $M^-$  peak, and should thereby increase sensitivity.

Currently, a number of ionization sources are being considered for use in a mass spectrometer-based explosives detector. Four of the sources are discussed in the following:

1. A low energy electron ionization source was developed at Sandia. This source uses a heated filament in a retarding electrical field. This source gives large currents of electrons with energies in the range of 0.2 eV. Success with the source was limited because either the electrons were too energetic or the temperature of the heated filament degraded the molecules.

2. An Atmospheric Pressure Ionization (API) source was assembled to check its sensitivity for explosives molecules. The source has tremendous sensitivity. Most of the molecules are in the  $M^-$  peak as opposed to being spread over the whole range of masses as fragments. This source is still being evaluated.

3. A corona discharge ionization source was designed and built by PCP, Incorporated, as a low energy electron ionizer for a mass spectrometer. One of these units was purchased and is being evaluated as another potential source.

4. A photoelectron ionization source is being considered as a possible candidate source. Photoelectrons from photons interacting with a metal should be low in energy and at atmospheric pressure should moderate very rapidly. A photoelectron source is being purchased from Quantatec International, Incorporated, for evaluation.

A "portable" mass spectrometer will be build

this fiscal year and will use one of the above ion sources.

#### **EXPLOSIVES VAPOR GENERATOR**

A calibrated explosives vapor source is needed for the evaluation of explosives vapor detectors. Problems with adherent vapors and accurate dilution of the vapors to the parts per trillion range have hindered the development of such a vapor generator. In 1982, a contract was placed with XonTech, Incorporated, to produce two calibrated vapor generators capable of delivering TNT vapors in concentrations ranging from 500 parts per billion down to 3 parts per trillion. These two units are now being more accurately calibrated in our laboratory.

#### **ACKNOWLEDGEMENTS**

The author wishes to acknowledge the following

persons for invaluable help in the Sandia National Laboratories (SNLA) Program: Professor M. White, University of Texas, Dr. Henry Peebles, Principle Investigator, University of Texas; and the following, all from Sandia National Laboratories: J. W. Rogers, preconcentrator work, Douglas C. Smathers, project leader and electrical work, Ms. Phyllis K. Peterson, vapor generator calibration, Pete J. Thoma, portal comparison, Richard Corn, mass spectrometer work and Jeffery B. McDowell, mechanical work.

#### **CONCLUSIONS**

This paper briefly describes the explosives detection program at Sandia National Laboratories. All vapor detection approaches that appear promising are being considered.



## TEMPERATURE DEPENDENCE OF ADSORPTION EFFECTS OF EXPLOSIVES MOLECULES

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**ABSTRACT.** Adsorption effects must be considered when selecting materials used for explosives vapor transport. Quartz, pyrex, Teflon, stainless steel and nickel adsorb explosives vapors at room temperature. The reduction in the adsorptive capabilities of these materials at elevated temperatures is discussed. Data were obtained by passing TNT, DNT, or PETN vapor through heat cleaned tubing. A gas chromatograph equipped with an electron capture detector was used for analyses. The temperatures needed to assure passage of explosives vapors range from 100–125°C for glass and quartz to 150°C for nickel, stainless steel, and Teflon.

### INTRODUCTION

Explosives vapor detection can be hindered by the tendency of these vapors to be adsorbed on cold surfaces. Such behavior was first observed in our laboratory during the evaluation of an explosives detector equipped with a Teflon inlet tube. It was observed that the instrument was unable to detect low concentrations of TNT vapor until the instrument was first "conditioned" by exposure to a very high concentration of TNT vapor. Later, we encountered adsorption problems when using metal tubing to transport explosives vapors in a vapor generator. We learned that the easiest way to circumvent these adsorption problems was to heat the transport tubing. A comparative study of various materials was made to determine the temperature at which these materials must be maintained in order to ensure efficient transport of explosives vapors. The materials evaluated were pyrex, quartz, Teflon, stainless steel, and nickel.

### EXPERIMENTAL PROCEDURE

Commercially available 1/8 inch and 1/4 inch outside diameter (OD) tubing was used in this study. Table 1 lists the types of tubing evaluated. The tubing was cut so all samples had the same internal surface area of  $2.65 \times 10^{-3}$  square meters (four square inches). Before evaluation, the tubing samples were degreased with solvent and heat cleaned at 250°C.

The clean tubing samples were placed in the oven of a Hewlett-Packard 5880 Gas Chromatograph (GC) where they served as a direct link from a 150°C injection port to a 200°C electron capture detector. Optimum performance of the electron capture detector was achieved by using 95% argon/5% methane as the carrier gas with a flow rate of 40 ml per minute.

A known nanogram quantity of explosive in acetone solution was injected into the tube while the oven was maintained at constant temperature

**Table 1. TUBING MATERIALS EVALUATED**

Material	Source	Size
1/4 inch OD* Stainless Steel	Supelco Cat #2-0527	0.53mm × 5.3mm ID**
1/4 inch OD Teflon (TFE)	Supelco Cat #2-0533	0.53mm × 5.8mm ID
1/4 inch OD Nickel	Supelco Cat #2-2709	1.35m × 2.1mm ID
1/4 inch OD Pyrex	Sandia Glass Shop	0.76m × 4mm ID
1/4 inch OD Quartz	Sandia Glass Shop	0.76mm × 4mm ID

\*OD = outside diameter

\*\* ID = inside diameter



at or above room temperature. This temperature was held for three minutes after injection and this allowed the solvent to clear the detector. If the explosive did not also pass through the detector within the three minute holding period, the GC oven was then heated to 200°C to drive off adsorbed explosive vapor.

For all materials, the initial data points were collected at 25°C using the aforementioned technique. The temperature was then increased by 25°C increments until the explosive peak appeared during the initial three minute holding time. Then smaller increments of 5°C or 10°C were used until a temperature was reached when the explosives vapors would pass through the tubing with the solvent.

Three explosives were used in this evaluation: Trinitrotoluene (TNT), Dinitrotoluene (DNT), and Pentaerythritol Tetranitrate (PETN). Purified samples were prepared at Sandia National Laboratories for this purpose.

TNT and PETN are commonly used explosives which are difficult to detect because of their low vapor pressures at room temperature; at 25°C TNT has a vapor pressure of 10 parts per billion and PETN has a vapor pressure of 10 parts per trillion. DNT is a higher vapor pressure impurity (750 parts per billion at 25°C) found in TNT; DNT contributes to the detectability of impure TNT.

### RESULTS

The data from this study are presented in Figures 1 through 3. Two plots are shown for each explosive; one shows percent retention versus temperature and the other shows retention time versus temperature.

The study was originally designed to produce

data for plotting percent retention versus temperature. Preliminary studies with Teflon tubing indicated that the percent retention would decrease with increasing temperature and that retention time would be an uninteresting variable. However, this was not the case with other tubing materials. With some combinations, the percent adsorption remained at a high constant value while retention time decreased with increasing temperatures. Therefore, both plots are presented to give a better picture of adsorption-temperature relationships.

In the Percent Retention versus Temperature Plots, the data are normalized with the amount of vapors adsorbed at 25°C assumed to be 100% adsorption.

For the Retention Time plots, the time given is a total of the three minute holding time and additional heating time at 20°C per minute. Retention times over three minutes are not actual values, but these numbers can be used to calculate the temperature at which the adsorbed explosive was driven from the tubing sample.

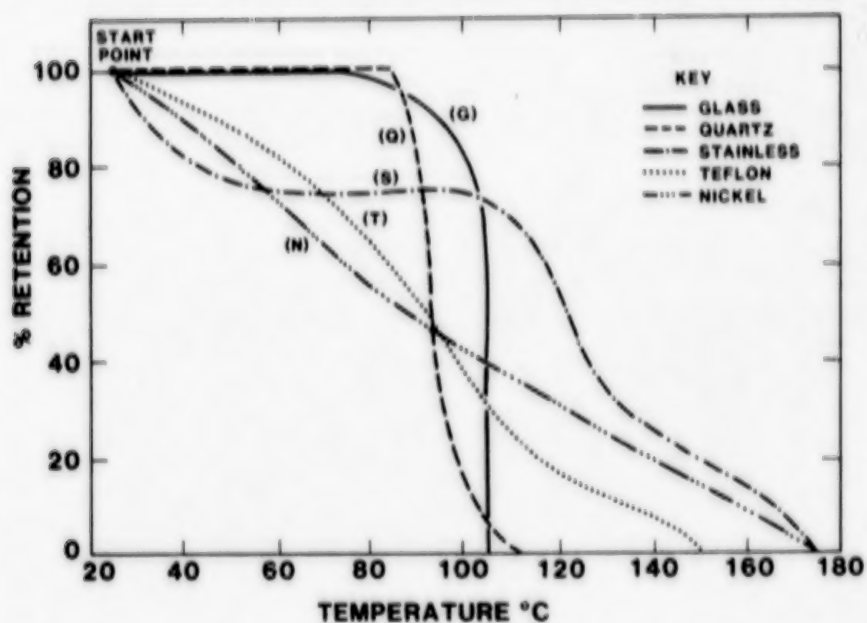
The plots show much variability with the different materials; this variability cannot be predicted *a priori*.

### CONCLUSIONS

Under laboratory conditions, tubing materials, such as, pyrex, quartz, Teflon, nickel and stainless steel were found to adsorb and retain explosives vapors. Our results suggest that glass and quartz should be heated to at least 100°C while Teflon, stainless steel, and nickel should be heated to at least 150°C in order to ensure the transport of TNT vapors. For the transport of PETN vapors, glass and quartz tubing should be maintained at an even higher temperature of 125°C.



# TNT ADSORPTION/TEMPERATURE



# TNT RETENTION TIMES

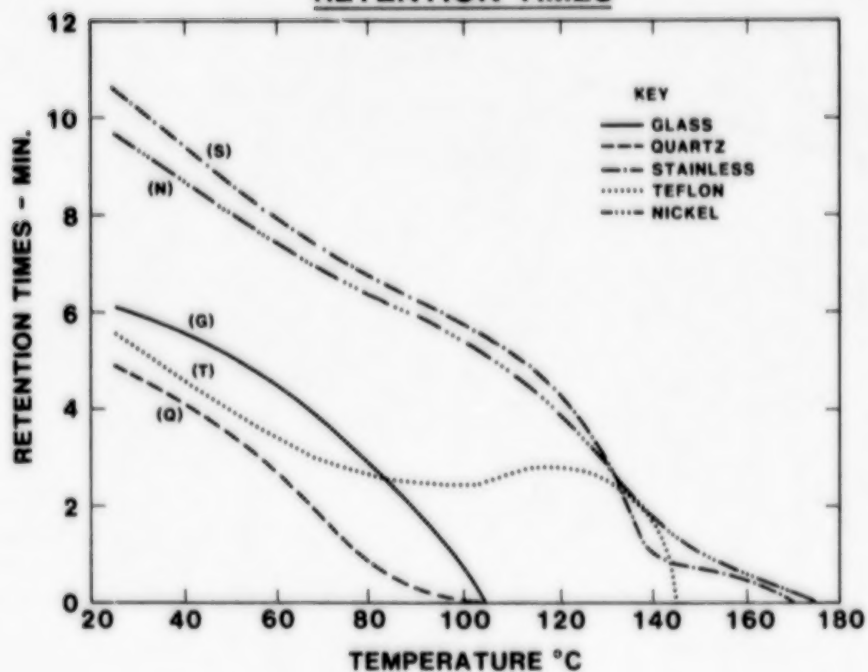


Figure 1. TNT adsorption characteristics on various tubing materials.

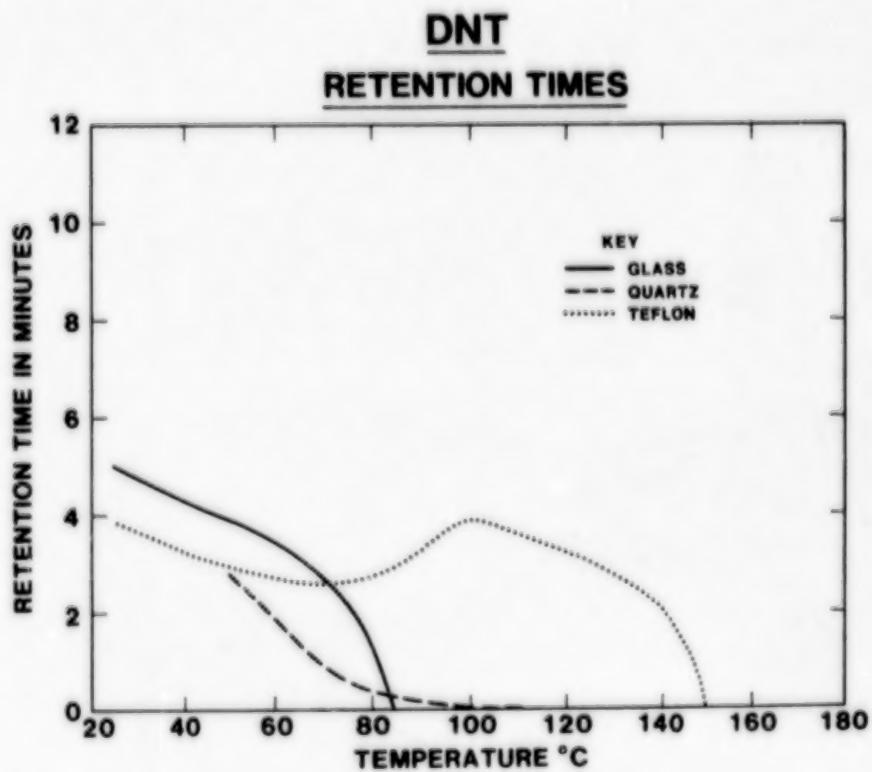
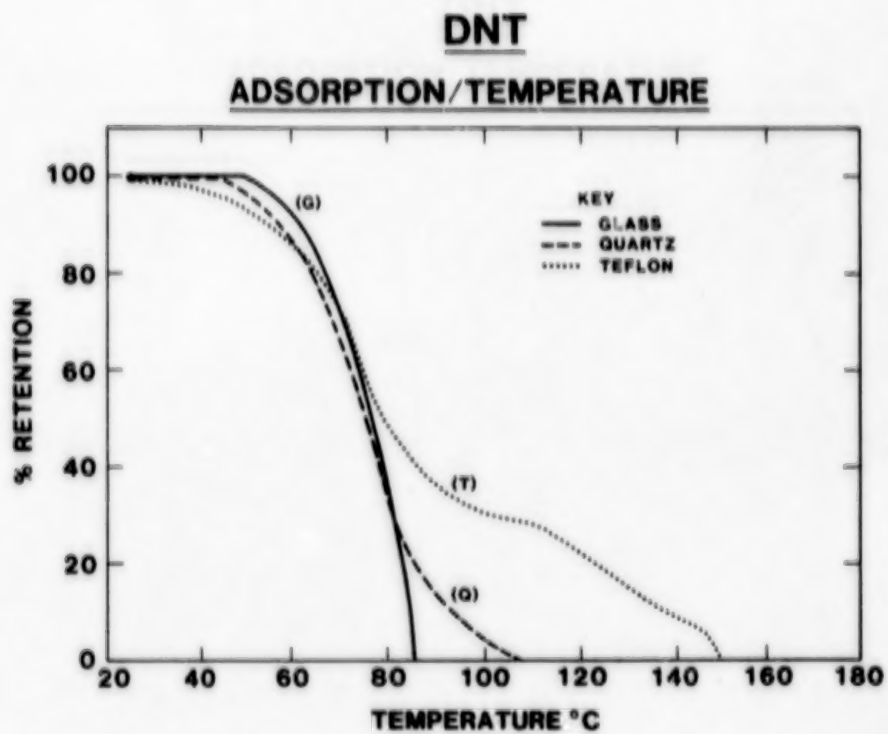


Figure 2. DNT adsorption characteristics on various tubing materials.

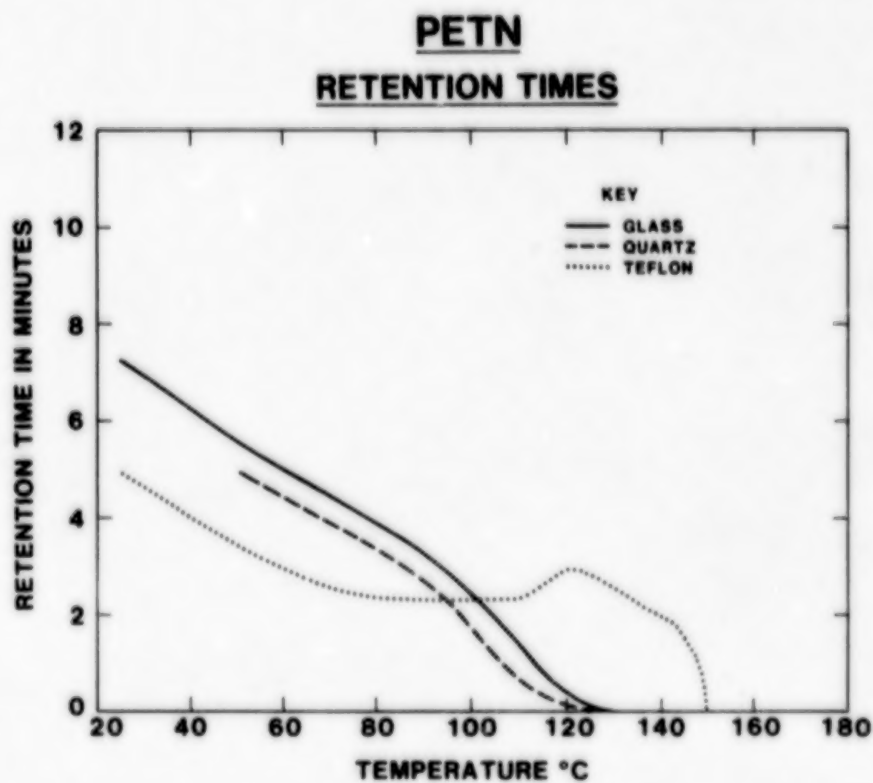
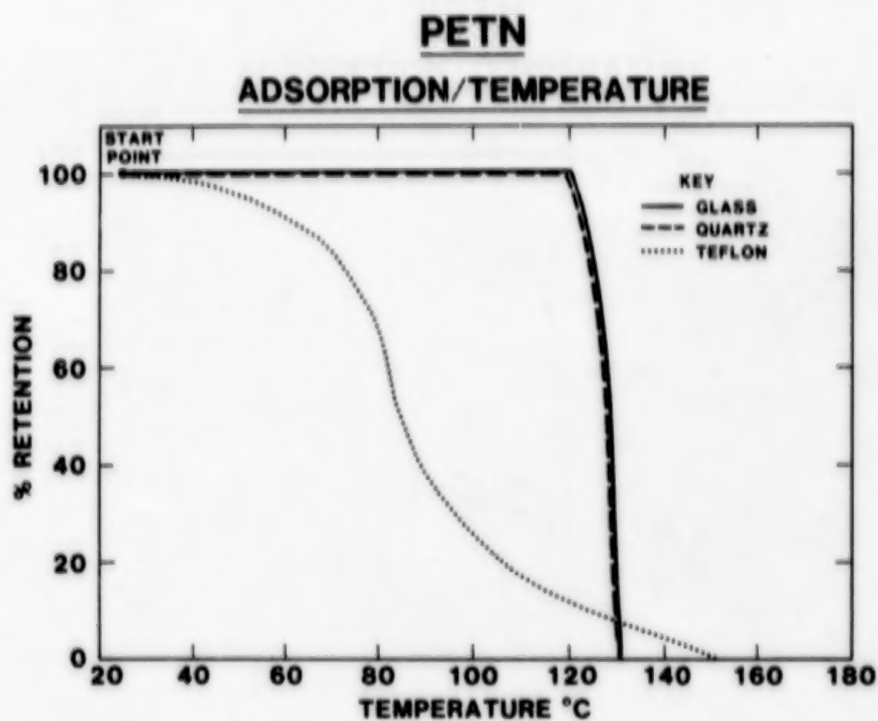


Figure 3. PETN adsorption characteristics on various tubing materials.



## THE SORPTION OF EXPLOSIVES ON HUMAN HAIR

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**ABSTRACT.** In the absence of bulk explosives, demonstration of illegal explosives involvement relies heavily on trace explosives contamination. In their most significant form traces will be closely associated with a suspect, for example on the hands. Such traces usually result from contact contamination, but experiments have shown that some common explosives constituents, for example ethylene glycol dinitrate (EGDN) have a sufficiently high vapour pressure to contaminate nearby objects via the vapour-phase. This opens up a wide area of study, some aspects of which are considered in a separate paper. Such contamination could be expected to occur on clothing, exposed skin and head hair, and it is the latter which will be discussed. Preliminary studies indicated that thermal desorption (ie. heating contaminated hair in a purge gas) gave variable recoveries of explosives vapour, and that adequate results were obtainable by solvent extraction despite some difficulties due to lipid. In subsequent experiments this recovery technique was used to study the influence of humidity, hair type and hair cleanliness on vapour uptake and persistence. The potential of hair contamination was assessed by exposing a volunteer to vapour from explosive and subsequently removing small hair samples for analysis. Identifiable traces of EGDN were recoverable for several hours after exposure. Aspects of this approach which would benefit from further work are incorporation of a clean-up, a population contamination survey and an informed review of the legal implications.

### INTRODUCTION

Many forensic laboratories regularly examine clothing, handswabs, surfaces in vehicles and other samples for explosives traces at or below the microgram level. Positive findings can generally be attributed to the contact transfer of solids or liquids either directly or indirectly, e.g. when contaminated hands convey explosives to other surfaces such as the edges of pockets. With certain explosives, such as gelignite, contamination by a different mechanism is possible owing to the emission of small amounts of characteristic vapour which could be sorbed and retained by exposed surfaces. A familiar example of this effect is the retention of tobacco smoke by clothing and hair. Contamination of hair by this means was studied in the present work because of its novelty and potential. The only comparable study appears to be the work of Baumgartner on the deposition of the abused drug phencyclidine on hair during its ingestion by smoking (Reference 1). The chemical

species chosen for the present work were ethylene glycol dinitrate (EGDN) and nitrobenzene (NB).

Hair presents some potential difficulties as an analytical substrate. Each fibre consists of an inhomogenous and complex mass of keratin fibres held in a keratin matrix (Reference 2), enclosed within a tough cuticle composed of up to ten layers of overlapping scales. The cuticle of animal fibres is known to form a barrier to molecules entering or leaving the fibre (Reference 3) and successful analysis of hair must either destroy it or allow for its effects. Hair may carry cosmetics residues and airborne dust in addition to natural secretions and cell scales, all of which could interfere with analysis. These problems have been encountered in the analysis of drugs of abuse in hair (Reference 1,4) and in the analysis of chlorinated hydrocarbons deposited in hair during growth (Reference 5). In each instance solvent extraction was employed, the hair sometimes being ground up, and this recovery technique seemed a promis-

ing one to evaluate. Thermal recovery, demonstrated by Chrostowski, Holmes and Rehn while working with explosion debris (Reference 6), has been found to work successfully for EGDN and NB on substrates such as PVC (Reference 7) and it was decided also to evaluate this method because it yields extracts free from involatile contaminants.

## EXPERIMENTAL

### Preparation of Hair Samples for Evaluation of Analysis

A large, relatively homogenous batch of hair was produced by mixing hair from a men's hairdresser using a compressed air jet. Because of the difficulty of uniformly spiking a hair sample with a known amount of EGDN or NB, much of the analysis evaluation was performed on a comparison basis using hair contaminated by exposure to the appropriate vapour. Various atmospheric concentrations of EGDN or NB were generated in a 15 l. bell jar using a perfusion tube containing EGDN or NB in conjunction with an exponential dilution system (Figure 1). Vapour concentrations in the jar were measured by drawing 500ml of air through a trap containing Tenax (R) and eluting sorbed EGDN or NB with 0.5ml ethyl acetate for

later analysis. The final validation experiments required samples of known composition and these were produced by adding 15  $\mu$ l. of a hexane solution of EGDN or NB to 2g of hair in randomly-distributed 1  $\mu$ l. increments. The spiked hair was left in a stoppered flask for three days to equilibrate before it was analysed.

### Analysis

Solutions containing EGDN or NB were quantified by gas chromatography (GC) with electron-capture detection using a glass WCOT column, coated with SE30, 50m  $\times$  0.5mm id. This was fitted with a splitter which passed 10% of the 0.5 $\mu$ l injection on to the column. The column temperature was 122°C and the nitrogen carrier flow rate was 1.5ml min<sup>-1</sup>. An integrator operating in the peak-height mode gave accurate retention times. Standard solutions were made up in hexane to cover the range 50 to 5000  $\mu$ l<sup>-1</sup>, using NB (BDH microanalytical reagent) and EGDN (PERME Waltham Abbey).

### Thermal Recovery

The hair sample of c 0.3g was placed in a glass test tube fitted with a modified Dreschel head (Figure 2) and the apparatus was kept at 95°C for

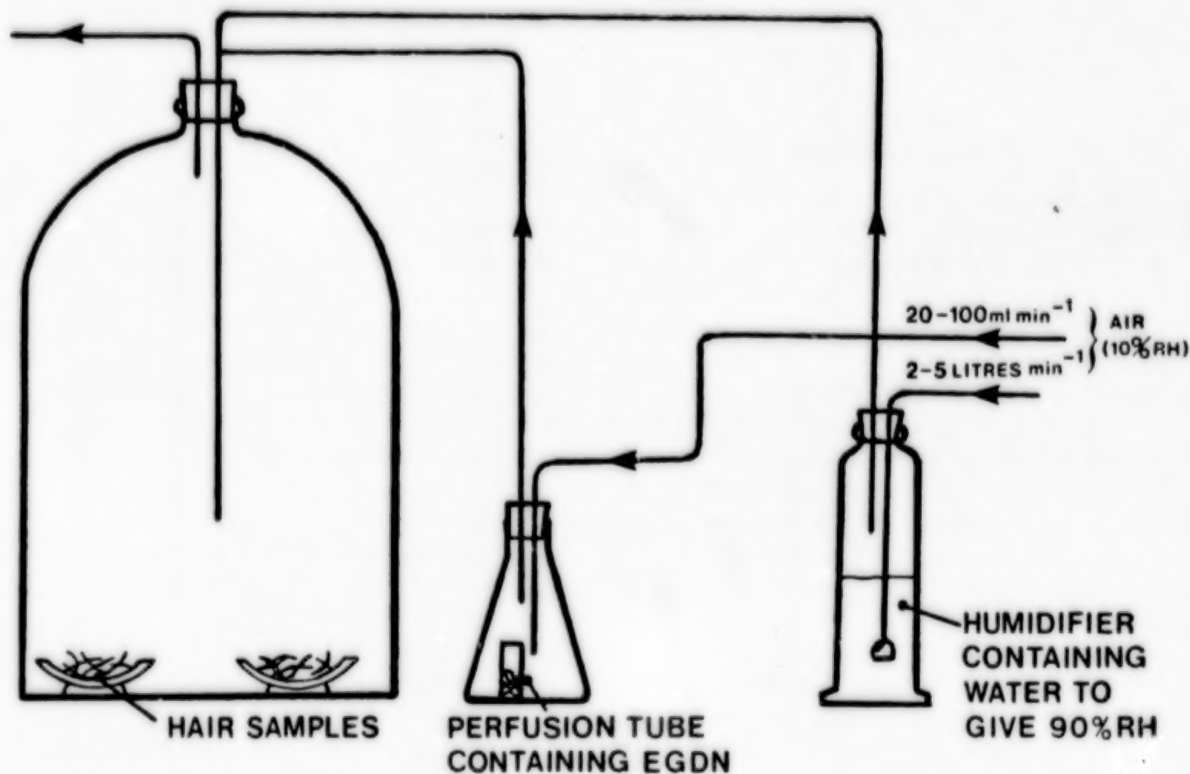


Figure 1. Exponential dilution system for exposing samples to known atmospheres.



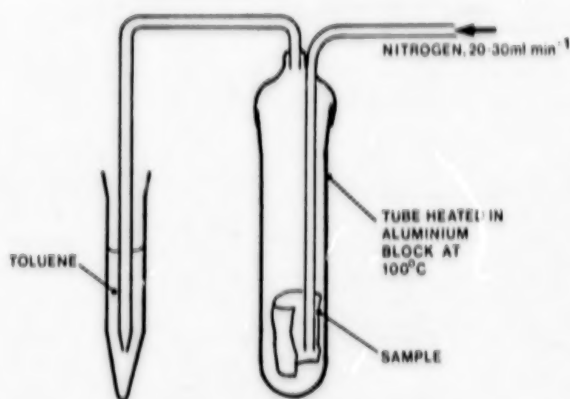


Figure 2. Apparatus for thermal recovery of volatile traces.

up to 6h while a nitrogen purge ( $25\text{ ml min}^{-1}$ ) carried evolved vapour to a second tube containing toluene. In some experiments water was added to the sample before heating in order to enhance recovery. Extracts were concentrated to 0.5–5ml by heating on a steam bath under a stream of air.

#### Recovery by Solvent Extraction

In initial experiments 0.7g portions of hair were extracted by soaking in 20ml hexane or toluene at  $20^\circ\text{C}$  for up to 96h and the solvent was removed by filtration and concentrated as described above. In subsequent analyses 0.3g of hair was extracted by soaking in 10ml of solvent at  $55^\circ\text{C}$  for up to 24h, and this method was used in the main experiments. In some instances the concentrated extracts were stored at  $-18^\circ\text{C}$  for 2h to freeze out co-extracted lipid and the solutions were analyzed before this re-dissolved.

#### Sorption Studies

The effects of hair type, ambient humidity and hair cleanliness on the amounts of EGDN and NB sorbed by hair were investigated. Because there are potentially many types of hair no comprehensive survey was attempted and instead one additional type was studied, female hair which had been curled by permanent waving. 'Clean' hair was prepared by washing bulked male hair with a shampoo, rinsing three times in water and allowing it to dry on filter paper. Humidity during exposure was held either at 10% relative humidity (RH) or 90% RH (Figure 1). The vapour concentrations studied ranged from  $0.6$  to  $20\text{ mg m}^{-3}$  and the exposure time for all samples was  $\frac{1}{4}\text{h}$ . After exposure hair samples were left in open air at approximately  $20^\circ\text{C}$  and 50% RH and samples were analysed at intervals.

Two larger-scale experiments were conducted.

In the first, a dummy head was constructed by fastening bulked male hair on to a 1 litre flask using adhesive tape and the flask was heated to  $36^\circ\text{C}$  by water circulation and exposed to gelignite vapour for  $\frac{1}{4}\text{h}$ . The vapour source was removed from the room and samples were analysed at intervals over the next few hours.

In the final experiment a male subject was exposed to gelignite vapour for  $\frac{1}{4}\text{h}$  and 0.3g hair samples were removed for analysis over a period of four days.

## RESULTS

### Recovery Experiments

The comparative experiments indicated that thermal recovery of EGDN was less efficient than solvent extraction (Table 1, experiment 1) and that no consistent improvement was attained by adding water (experiments 2 and 3). Because a general recovery method was required thermal recovery of NB from hair was not examined and further work concentrated on solvent extraction.

The results (Table 2) indicated that even at  $55^\circ\text{C}$  an extraction time of at least 3h was required for efficient recovery of both EGDN and NB. There was no advantage in using toluene rather than hexane and so the latter was used in subsequent analyses because of its convenience and lower toxicity. Grinding hair before extraction gave a reduced recovery of EGDN and of NB.

### Effects of Hair Type, Cleanliness and Humidity on Vapour Sorption

The amounts of EGDN and NB sorbed by hair under various conditions were not determined by measurement immediately after exposure because the concentration of sorbed material altered rapidly at that stage. Instead, samples from each exposed batch of hair were analysed at intervals of several hours and the 5–6 results so obtained were plotted as a graph of time versus log concentration. A linear relationship was found for each set of results (e.g. Figure 3), indicating that the concentration of sorbed material decayed according to first-order kinetics. By extrapolation the initial concentration  $C_0$  was obtained for each experiment and this was used as a basis for comparing the effects of humidity etc. The decay constant or half-life  $t_{1/2}$  was also calculated for each set of results and its reliability was estimated by calculating Student's  $t$  and comparing it with tables of the  $t$ -distribution.  $C_0$ ,  $t_{1/2}$  and the statistical significance for each experiment are listed in Tables 3–5.

**Table 1. RECOVERY OF EGDN FROM HAIR EXPOSED TO EGDN VAPOUR**

Sample Batch No.	Recovery method	EGDN recovered, ng mg <sup>-1</sup>
1	thermal 0-3h	0.6
	3-6h	0.004
1	thermal 0-3h	0.7
	3-6h	0.008
1	hexane extraction, 24h at 20 °C	1.65
2	thermal 0-3h	2.6
	(2ml water added)	
2	hexane extraction, 24h at 20 °C	2.8
3	thermal 0-3h	0.4
	(2ml water added)	
3	hexane extraction 96h at 20 °C	1.0

**Table 2. RATE OF SOLVENT EXTRACTION OF ADDED EGDN/NB AT 55 °C**

Sample hair sample analyte added	Extraction conditions	Extraction time hours	Amount recovered	
			ng mg <sup>-1</sup>	as cumulative % of added amount
EGDN, 9.0ng mg <sup>-1</sup>	unground sample, hexane	0-1	6.9	76
		1-3	2.1	100
		3-24	0.5	105
EGDN, 9.0ng mg <sup>-1</sup>	ground sample, hexane	0-1	4.2	46
		1-3	1.6	64
		3-24	0.5	64
NB, 15ng mg <sup>-1</sup>	unground sample, toluene	0-1	9.4	62
		1-3	2.5	79
		3-24	1.0	85
NB, 15ng mg <sup>-1</sup>	ground sample, toluene	0-1	6.1	40
		1-3	2.2	48
		3-24	0.5	51
NB, 15ng mg <sup>-1</sup>	unground sample, hexane	0-1	8.8	58
		1-3	2.4	74
		3-24	2.3	89

Table 3. SORPTION AND RETENTION OF EGDN AND NB BY UNWASHED MALE AND FEMALE HAIR

Exposure vapour (Conc mg m <sup>-3</sup> )	Hair	C <sub>0</sub> ng mg <sup>-1</sup>	t <sub>1/2</sub> h	Level of significance P
EGDN (1)	Bulked male	5.7	15	0.05
EGDN (1)	female	5.1	22	0.01
NB (2)	bulk male	3.7	72	0.1
NB (2)	female	13.0	43	0.05
NB (2)	abraded bulked male	5.6	98	0.1

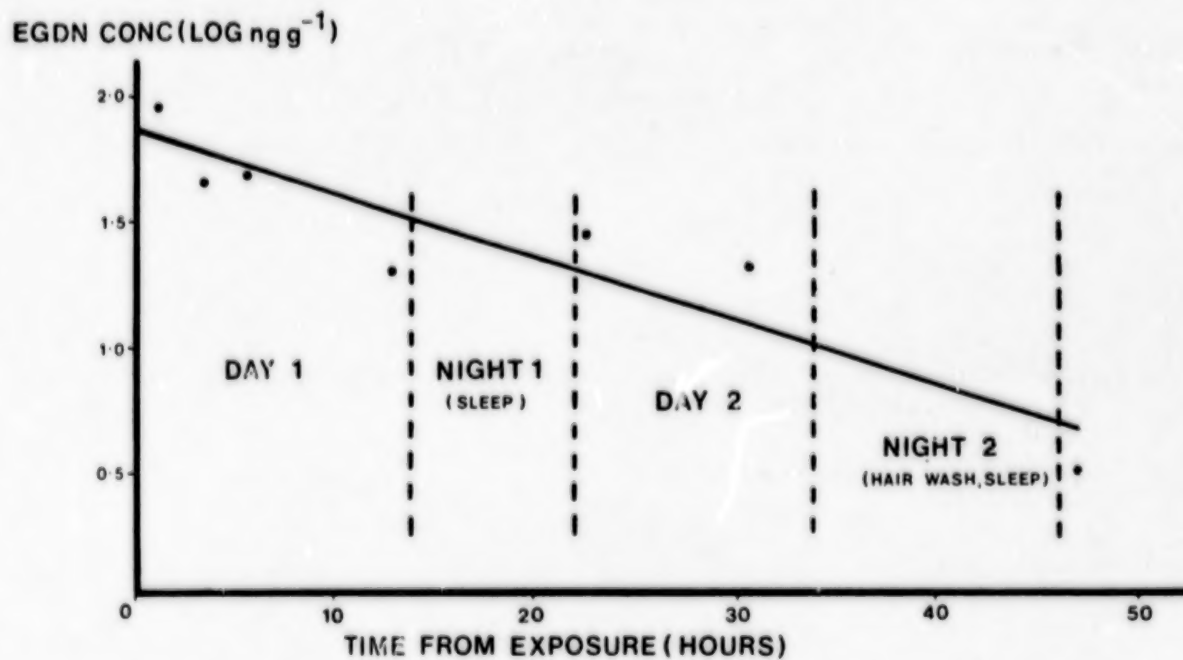


Figure 3. EGDN persistence in the hair of a volunteer.

The results in Table 3 suggest that the two types of hair studied had a similar affinity for EGDN,  $C_0$  for each being c  $5 \text{ ng mg}^{-1}$ . In contrast appreciably more NB was sorbed by the female hair than by the male hair and this effect was not reproduced by abrading male hair before exposure.

The effects of washing also varied according to the chemical species sorbed (Table 4). There was no difference between the amounts of NB taken up by unwashed and washed bulked male hair,  $C_0$  for each being  $13 \text{ ng mg}^{-1}$ , but unwashed bulked

male hair sorbed  $5.7 \text{ ng mg}^{-1}$  of EGDN compared to only  $2.6 \text{ ng mg}^{-1}$  of EGDN sorbed by washed hair.

The ambient humidity during exposure affected sorption of both EGDN and NB in the same way, more vapour being taken up in high humidity than in low humidity (Table 5). The statistical significance of both sets of NB results was poor ( $P > 0.1$ ) but the effect of humidity was consistent with the more reliable EGDN observations.

Table 4. SORPTION AND RETENTION OF EGDN AND NB BY UNWASHED AND WASHED MALE HAIR

Exposure vapour (conc $\text{mg m}^{-3}$ )	Pretreatment	$C_0$ $\text{ng mg}^{-1}$	$t_{1/2}$ h	Level of significance P
EGDN (1)	Unwashed	5.7	15	0.05
EGDN (1)	washed	2.6	36	0.1
NB (20)	unwashed	13.0	38	0.05
NB (20)	washed	13.0	48	0.05

Table 5. EFFECT OF AMBIENT HUMIDITY ON SORPTION OF EGDN AND NB BY MALE HAIR (SAMPLES EXPOSED TO 50% RH AFTER EXPOSURE)

Exposure vapour (conc $\text{mg m}^{-3}$ )	Humidity during exposure %RH	$C_0$ $\text{ng mg}^{-1}$	$t_{1/2}$ h	Level of significance P
EGDN (0.6)	90	1.2	25	0.05
EGDN (0.6)	10	0.3	56	0.05
NB (2)	90	3.7	72	$>0.1$
NB (2)	10	0.7	32	$>0.1$

## Persistence

The decay half-lives from the small experiments (Table 3-5) are summarised in Table 6. The mean of the  $t_{1/2}$  values for EGDN was 28h and for NB the mean  $t_{1/2}$  was 51h; using the  $t$ -test (with the Bessel correction for small number of results) this difference was found to be significant ( $p = 0.05$ ).

Table 6. SUMMARY OF DECAY HALF-LIVES

Substance	$t_{1/2}$ hrs	Level of significance
EGDN	15	0.05
	22	0.01
	15	0.05
	36	0.1
	25	0.05
	56	0.05
NB	72	0.1
	43	0.05
	38	0.05
	48	0.05
	72	0.01
	32	0.1

EGDN persistence results from the experiments with the dummy head and with a volunteer yielded the reduced  $t_{1/2}$  values of 7h (not significant at the  $p = 0.1$  level) and 11h (highly significant,  $p = 0.01$ ). The reduced  $t_{1/2}$  values was attributed to the higher hair temperature in these experiments.

## DISCUSSION

At the commencement of this study it was suspected that any EGDN or NB taken up by hair would be sorbed at the fibre surface, perhaps dissolved in a lipid coating. This simplistic picture is incorrect, as shown by the considerable time necessary for solvent recovery, *i.e.* at least 3h at 55°C, which is probably due to the slow migration of molecules from within the fibre to its surface. The increased thermal recovery obtainable by adding water also suggest retention within the fibre; presumably the high humidity causes the fibres to swell and increases the permeability of the cuticle. The enhanced amounts of vapour taken up during exposure in a high ambient humidity is also attributable to this effect.

EGDN or NB could be retained in a lipid phase held within the fibre, but interaction with fibre keratin is also possible. If solution in a lipid phase were the principal mechanism the vapour pressure of EGDN and NB (EGDN 0.049mm Hg at 20°C

(Ref 9); NB 0.22mm Hg at 20°C (from extrapolation of data in Reference 9)), would be reduced to  $P_c$  according to Raoult's Law,

$$P_c = x_c P_0$$

where  $P_0$  is the vapour pressure and  $x_c$  is the concentration of the sorbed species expressed as a mole fraction. Although much reduced, the vapour pressures of EGDN and NB would still bear the same relative volatility, *i.e.* NB would be the more volatile. NB would therefore be expected to be lost more rapidly from hair than EGDN, but the reverse was observed in practice, the mean  $t_{1/2}$  for EGDN being 28h and the mean  $t_{1/2}$  for NB being 51h. This suggests that the molecules interact with the hair fibre itself, NB binding more strongly than EGDN. The different effects noted with unwashed/washed hair and male/female can then be explained as follows: (1) EGDN is mainly held in the hair lipid phase, the amount of which is reduced by washing, and (2) NB is mainly held by hair keratin and female hair sorbed more NB by virtue of structural differences possibly induced by permanent waving.

Persistence on live subjects has only been studied briefly using EGDN, and the half-life of 11h obtained with EGDN suggests that hair analysis is potentially useful. Aspects which remain to be studied include sorption mechanisms, potential interferences and legal implications.

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## A NOVEL METHOD FOR THE RECOVERY OF VOLATILE EXPLOSIVES TRACES

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**ABSTRACT.** Although trace explosives contamination can sometimes be detected with an explosives vapour detector, further positive identification is usually necessary. For reasons of practicality this will generally involve recovery of the explosives traces from the substrate, ideally without co-extracting other materials which could interfere with analysis. When recovering volatile explosives such contamination can be minimised by employing high-temperature vapour-stripping, in which a purge gas transfers desorbed vapours to a suitable trapping arrangement. If rapid screening of several items such as clothing is required, or where the sample is large, such as a vehicle, thermal recovery using conventional laboratory apparatus is inappropriate, and to overcome this problem portable recovery equipment has been devised. This consists of a heated platen which is placed in contact with the surface, an air pump and a trap containing Tenax (R), a polymeric absorbent. In validation experiments this device recovered ethylene glycol dinitrate (a constituent of commercial gelignites) and other explosives vapours from a variety of substrates. In most instances it was much more efficient than solvent-swabbing, the main alternative. With a sampling time of five minutes the limit of detection was 5 ng per square centimetre. At this level of sensitivity the forensic scientist can recover traces resulting from vapour-phase contamination, in addition to the contamination resulting from contact or from explosion, and the technique has been successfully used in a number of forensic cases.

### INTRODUCTION

There are two basic situations in which trace analysis of explosives may arise. Post-detonation debris is examined to identify the type of explosive involved, and although quite large amounts of explosive may be present, trace techniques are usually required. Examinations also attempt to establish whether there is any evidence linking suspects, or their clothing, premises and vehicles with the illegal usage of explosives, and this too requires trace analysis. In either situation it is sometimes possible to obtain a rapid indication of explosives contamination using a suitable explosives vapour detector such as the Analytical Instruments AI70 or the Pye PD3, but these can best be regarded as a potential shortcut in defining contaminated areas rather than as a substitute for analysis. At present chemical analysis requires extraction of explosives from a contaminated object, usually by solvent extraction or swabbing with cotton-wool

and solvent. Provided suitable solvents are employed these recovery techniques are applicable to a wide range of explosives, but they tend to give 'dirty' extracts containing co-extracted material which may interfere with or prevent analysis. One answer is to incorporate a suitable clean-up, for example that of Douse (Reference 1), but a better alternative is to employ a clean recovery technique in the first place. If the explosives traces are volatile, as will be the case when the commonly misused gelignite explosives are involved, thermal recovery is possible, and this has the enormous advantage of yielding clean samples for analysis. This technique was first demonstrated by Chrostowski, Holmes and Rehn (Reference 2) who recovered explosives such as TNT which had been added to sand by heating the mixture while drawing air through it. We have adapted the technique to permit semiquantitative analysis of samples containing nanogram amounts of ethylene glycol

dinitrate (EGDN), a constituent of gelignites, while for field use we have developed a portable recovery device which we refer to as the contact-heater. The contact-heat permits rapid recovery of volatile explosives and is particularly useful when examining large items such as an overcoat or a vehicle.

## THE CONTACT-HEATER

### Description

This equipment consists essentially of a platen heated to 100°C which is placed against the sample and a pump which draws air through a hole in the platen (Figure 1). To avoid marking the sample surface the platen is spring-loaded to limit the pressure which can be applied. The air passes through a glass tube containing Tenax, a proprietary absorbent, which retains vapours emitted by the sample. These substances are then eluted from the Tenax trap using 0.3ml of ethyl acetate for analysis by gas chromatography (GC) or mass spectrometry.

In use, the unit is switched on and reaches operating temperature within 5 minutes. A previously blanked and conditioned Tenax tube is fitted and the device is kept in contact with the sample surface. After sampling for 2-5 minutes the Tenax tube is removed for laboratory examination. If the sample is damp a simple condenser to remove excess water can be fitted (Figure 2). When examining grossly contaminated samples the contact-heater itself becomes contaminated with explosives. Cross-contamination is guarded against by a bake-out at 120°C and by replacing the PTFE tubing linking the platen to the Tenax trap. As a final check, it is advisable to run blanks before important examinations. Existing models of the contact-heater have been designed and constructed at RARDE and commercial fabrication is now in progress.

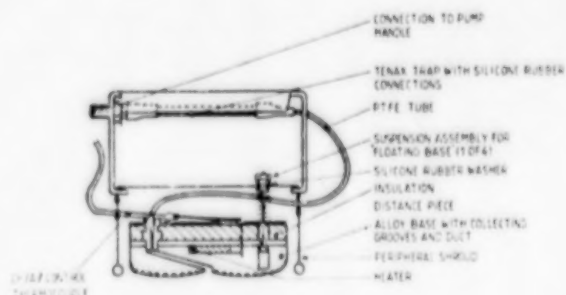


Figure 1. Section of contact heater

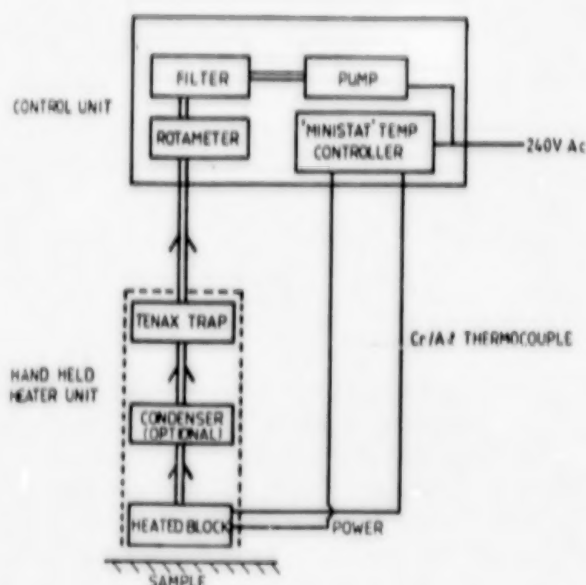


Figure 1A. Block-diagram of contact heater

### Performance trials

An indication of the performance when examining residues from a gelignite explosion can be obtained from Figures 3 and 4. The first

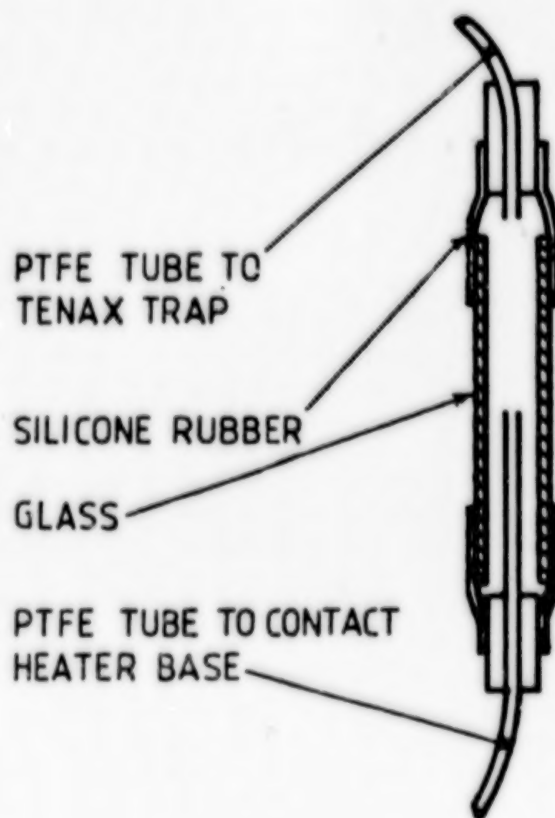


Figure 2. Improved condenser

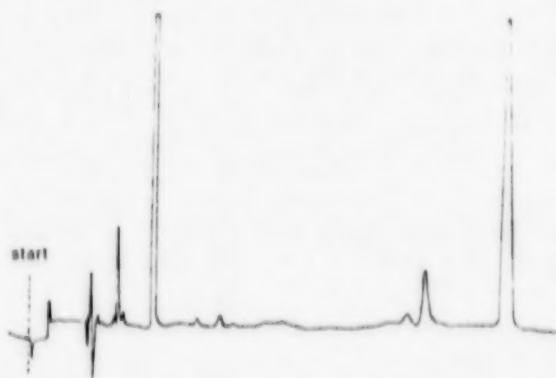


Figure 3. GC trace of contact heater extract of paper adjacent to a gelignite explosion (0.2ul ex 0.2ml)

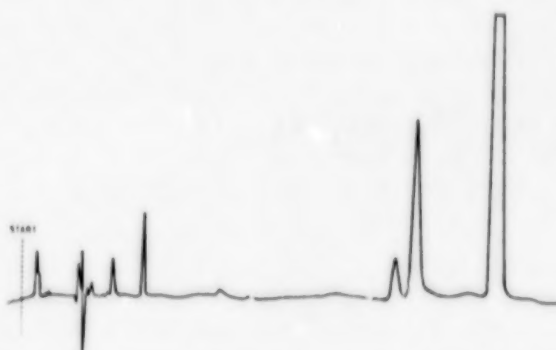


Figure 4. GC trace of ethyl acetate extract of 15cm<sup>2</sup> of paper adjacent to gelignite explosion (0.2ul ex 5ml)

chromatogram shows residues recovered by using the contact-heater for five minutes on a piece of thick paper located near an explosion. The second GC trace shows the material recovered by an ethyl acetate extraction of another portion of the same paper. The traces are qualitatively very similar and include both EGDN and nitroglycerine (NG), but the amounts present vary because thermal recovery favours the more volatile EGDN.

To compare contact-heater performance with that of the most likely recovery technique to be used in practice, solvent swabbing, a piece of plasticised upholstery PVC 0.5mm thick was exposed to EGDN vapour and was examined after 36h in open air. Swabbing was performed by wetting 25mg of cotton wool with diethyl ether, shaking it once and applying the swab to 25cm<sup>2</sup> of the PVC, making three passes over the surface. The swab was then eluted with 1.5ml of ethyl acetate. Analysis of this extract failed to detect EGDN. A second 25cm<sup>2</sup> area was swabbed successively with 25 swabs, and these were analysed in batches of five, the extracts being concentrated to 0.3ml before GC analysis. Swabs 1-5 yielded a

small peak corresponding to approximately 70pg of EGDN per injection, but analysis of the other swabs showed that this represented only a small portion of the EGDN present on the PVC; even swabs 20-25 contained an amount of EGDN comparable to the amount in swabs 1-5. Using the contact-heater on the same PVC gave vastly improved sensitivity to EGDN (Figure 5), indicating that the technique is one to two orders of magnitude more sensitive than single ether swabbing.

The efficiency of contact-heater recovery of EGDN was quantified by placing gelignite cartridges in a saloon car to contaminate it, and then using the device to examine the various interior furnishings for EGDN over a period of three weeks. For reference purposes the total EGDN in carpeting, seat PVC etc was determined by heating 5cm<sup>2</sup> of sample for 2h at 100°C using the apparatus shown in Figure 6. Nitrogen (25ml min<sup>-1</sup>) was passed through a heated tube containing the sample in order to carry desorbed EGDN into a second tube containing toluene. In earlier experiments we have found that this technique recovers 80% of EGDN present in upholstery materials. The results showed that virtually all exposed surfaces had taken up EGDN vapour from the car atmosphere, the amounts present being of the order of 10ng cm<sup>-2</sup>. After removal of the explosive the concentrations of sorbed EGDN diminished according to first order kinetics; a typical set of results is shown as a semi-log graph in Figure 7. These results provided a yardstick for contact-heater recovery of EGDN and permitted the percentage recovery of EGDN from different surfaces to be calculated. Table 1 shows that the recovery with 5 minutes sampling time was typically 8% of the amount of EGDN present. There is only slight evidence that this efficiency diminished as the interval between exposure and analysis grew

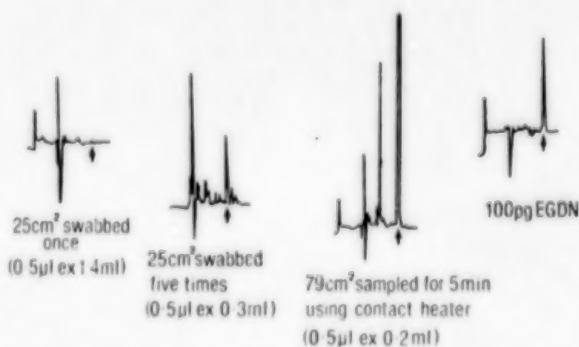


Figure 5. GC traces of EGDN recovered from contaminated 0.5mm thick PVC

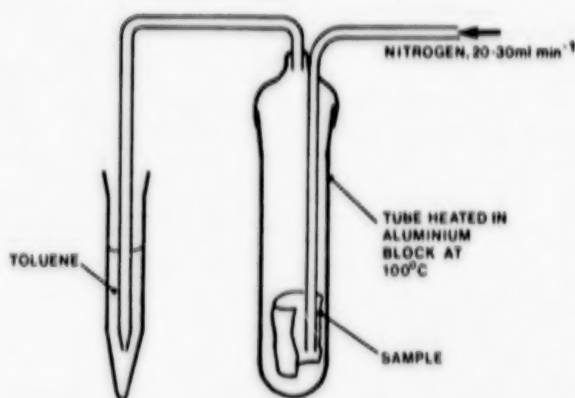


Figure 6. Apparatus for thermal recovery of volatile traces

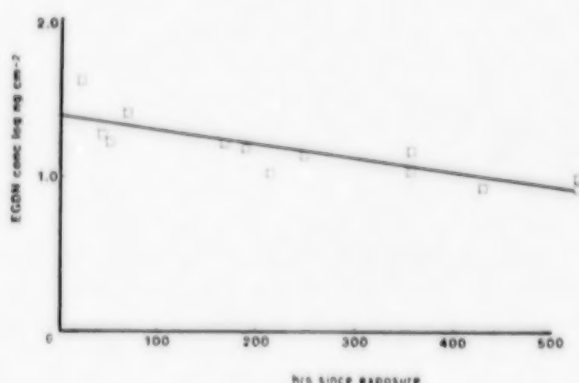


Figure 7. EGDN persistence in seat PVC

longer. The lowest total concentration of EGDN found on any surface was  $5 \text{ ng cm}^{-2}$ , and this was easily detected with the contact-heater.

Table 1. RECOVERY OF EGDN FROM PVC AND CARPET USING THE CONTACT-HEATER

Hours since exposure	% recovery from door PVC	carpet
40	17	5
100	7	—
200	8	—
350	8	5
500	—	9
700	9	8

This comparatively high recovery, combined with the small volume in which recovered explo-

sives is made available for analysis accounts for the very high sensitivity of the technique when compared to swabbing.

### Performance in practice

The contact-heater has been used in connection with a number of vehicles involved in explosions. EGDN traces were found in all exposed surfaces in cases where the use of gelignite was suspected. The site of one explosion thought to have involved TNT was also examined, but no significant traces were found. Exposure to explosives in the absence of any explosion has also been demonstrated using the contact-heater. In one instance an item of luggage recovered after submersion in water was found to be grossly contaminated and EGDN, NG and dinitrotoluenes were recovered and identified, showing that it had contained gelignite. In another case a motor car was shown to be contaminated with EGDN, thus linking it with explosives, even though conventional chemical examination using swabbing and a vapour detector yielded no evidence of explosives.

### CONCLUSION

A very wide range of materials may be involved in explosives cases, and the contact-heater recovery technique can only assist with identification of those which are volatile. However, the speed, convenience and sensitivity of the contact-heater, combined with the frequent usage of explosives containing volatile constituents make it an attractive additional tool for the forensic analyst.

### ACKNOWLEDGEMENTS

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## THE INSTANTANEOUS DETECTION OF EXPLOSIVES BY TANDEM MASS SPECTROMETRY

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**ABSTRACT.** The TAGA 6000 Tandem Mass Spectrometer (MS/MS) coupled with an atmospheric pressure chemical ionization (APCI) source provides a non-invasive method of detecting vapors from explosives in a variety of scenarios. The APCI source, fitted with appropriate sampling lines, allows instantaneous detection of these vapors in the sub-ppb (parts-per-billion) concentration ranges. The tandem mass spectrometer portion of the instrument provides a highly specific analysis of the vapors which are detected. The first mass analyzer of the MS/MS system is used as a separator which separates the ions formed from the various components of the sampled air according to their molecular weight. These ions are fragmented in a collision region, and the second mass analyzers used to determine which fragment ions are formed. The fragment ion spectrum of a compound is a "fingerprint" of that component which can be used for the identification of the component from a spectral library. Applications of the APCI/MS/MS technique to the detection of several explosives will be presented. Nitroglycerine, in the form of dynamite and double-base propellants, has been detected on aircraft, on the human body, in sealed cardboard boxes, in a mocked-up cargo container and on a cleaned revolver. Involatile explosives such as C4 can be detected from the vapors given off by solvents (cyclohexanone) or impurities. Remote sampling for relatively involatile explosives or for particles from explosives is accomplished using a hand-held probe concentrator which traps the vapors or particles on an organic coating. The sampling probe may be sealed and returned to the TAGA MS/MS system for analysis. Customized computer software allows for near "black-box" operation of the system for non-technical operators. Descriptions of the instrument, sampling techniques, software and applications related to explosive detection will be presented.

### INTRODUCTION

The two primary characteristics required of any viable explosives vapors detector are sensitivity and specificity. State-of-the-art detectors are capable of responding to parts-per-trillion concentration of explosive vapors; this must be regarded as a minimum requirement in view of the exceptionally low vapor pressures of the plastic and water-gel explosives. It is clear that when working at such low levels the detector must also show exceptional specificity in order to prevent an unacceptable level of false alarms. In most practical

applications the detector must also demonstrate a fast response time.

SCIEX has been involved since its inception in the instantaneous detection of ultra-trace concentrations of vapors. The approach we have taken has utilized Atmospheric Pressure Chemical Ionization (APCI) with quadrupole mass spectrometer analysis and detection. APCI provides for ppt detectability and moderate specificity of ionization. Since the air sample is drawn directly into the ion source at approximately 1.5 liters/second, the detector shows essentially instantaneous response.

The mass spectrometer provides the specificity of molecular weight information. It should be noted that the sensitivity of the system can be enhanced by pre-concentrating the sample, for example on a coated adsorber wire or tenax trap followed by flash desorption into the ion source.

One of the most significant recent advances in mass spectrometry is the development of the tandem mass spectrometry technique. In the SCIEX approach, three quadrupoles are interfaced on axis, communicating with the APCI ion source at one end and the electron multiplier detector on the other. After ionization, the sample ion matrix is extracted through the atmosphere-vacuum interface and focussed into the first quadrupole analyzer. Ions of a particular mass/charge ratio, the "parent" ions, are filtered from the matrix and injected directly into the second quadrupole region. The second quadrupole acts as a confinement cell in which the parent ions are caused to collide with a molecular beam of neutral argon atoms. The parent ions thereby undergo Collision Induced Dissociation (CID), yielding "daughter" ions which are fragment ions characteristic of the structure of the parent ions. The daughter ions are transmitted into the third quadrupole region where they undergo mass analysis, giving rise to a characteristic daughter ion spectrum. The analytical scheme is shown in Figure 1. It should be clear that, in general, the MS/MS analysis provides a much higher specificity of analysis than a single MS.

## EXPERIMENTAL

Most of the data presented here were obtained using the commercial TAGA 6000 tandem mass spectrometer system with APCI source. Explosive samples (which, regrettably, were several years old) were cut or disturbed to expose a fresh surface. The samples were placed in a vial, and the vial inserted in a glass "T" over which approximately 1.5 l/second of room air was drawn. The entire air sample was introduced directly to the ion source through a 30 cm. glass sample line. No attempt was made to heat-trace the sample line, and no attempt at quantitation was made.

The ambient air sample serves as the reagent gas for the ion source. In some instances chloroform was added at the ppm level to generate chloride reagent anions.

Single MS experiments were performed by operating the second and third quadrupoles in the rf-only mode; mass analysis was performed only in the first quadrupole. MS/MS results were obtained by mass-analyzing in both the first and third quadrupoles.

The TAGA 6000 operates in either the positive ion mode or negative ion mode by the application of appropriate focussing potentials in the source, analyzer and detector regions.

## RESULTS

Previous work (Buckley *et al.* (1978)) has shown that nitroglycerine (NG), ethylene glycol dinitrate

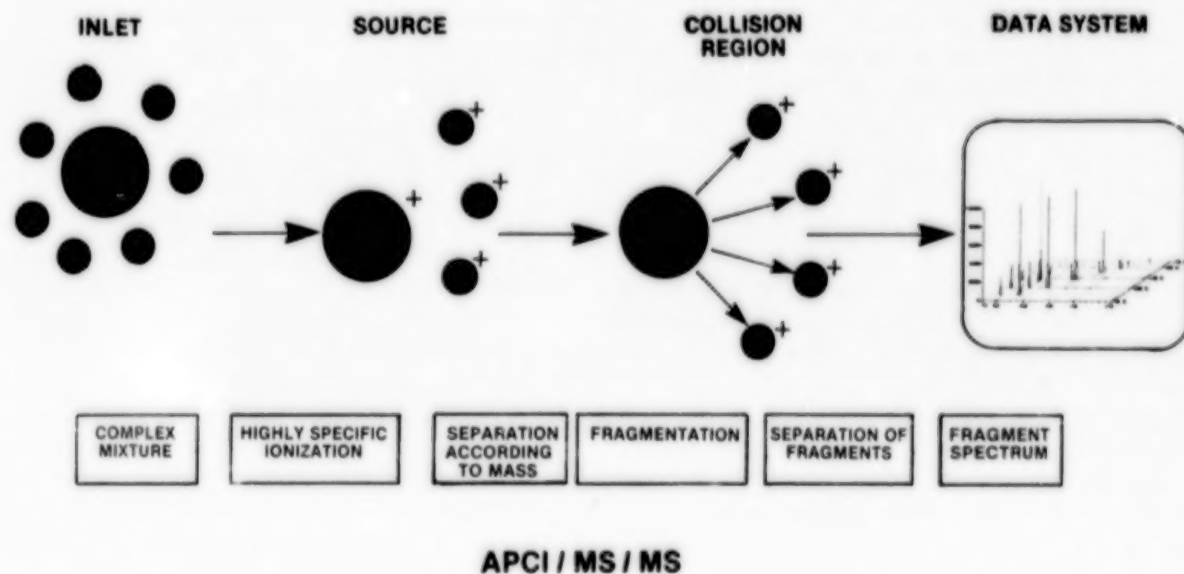


Figure 1. Schematic of analysis of ambient air by APCI/MS/MS.



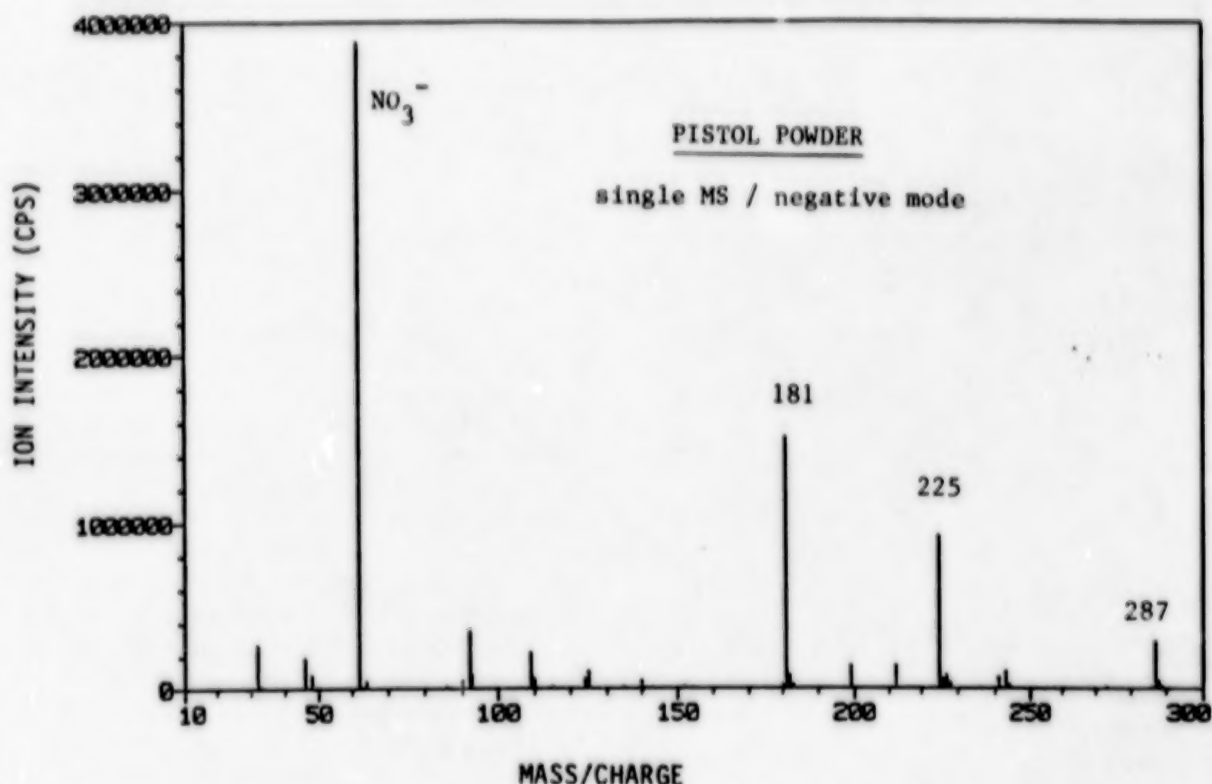


Figure 2. Single MS spectrum (negative mode) of the headspace volatiles above double-base pistol powder.

(EGDN), dinitrotoluene (DNT) and trinitrotoluene (TNT) are most sensitively detected in the negative ion mode. An additional advantage of this is that, in general, less interference is observed in the negative mode due to the higher specificity of negative ionization under APCI. The single MS (negative mode) spectrum of the volatiles emanating from double-base pistol powder is given in Figure 2.

The most prominent responses are observed at  $m/z = 62$ , 181, 225 and 287. A smaller response at  $m/z = 227$ , corresponding to the molecular ion ( $M^-$ ) of the NG is observed. The large response at  $m/z = 62$ , corresponding to  $\text{NO}_3^-$ , is a typical fragment ion of organonitrate compounds (notably EGDN), but is considered not to be specific enough to trigger an alarm for explosives. The CID spectra of the remaining ions were recorded in order to assist in the identification of these vapors, and are given in Figure 3.

Both the parents at  $m/z = 181$  and 225 give rise to predominant  $\text{NO}_3^-$  with a less intense  $\text{NO}_2^-$  peak. As such, one can conclude that each corresponds to an organonitrate species; they may be assigned to NG, assuming the loss of  $\text{NO}_2$  and  $\text{H}_2$  in the ionization process, respectively. On the other hand, the  $m/z = 287$  parent ion yields essen-

tially only the  $\text{CO}_3^-$  daughter ion at  $m/z = 60$ ; the  $m/z = 287$  parent ion clearly corresponds to the cluster ion  $(\text{NG} \cdot \text{CO}_3)^-$  formed as a primary product in the ion source. The observation of this cluster ion leads one to conclude that the most sensitive approach to the detection of NG might be to induce such a clustering reaction. Chloroform was added to the ambient air sample to generate reagent  $\text{Cl}^-$  ions. The single MS spectrum observed under these conditions is shown in Figure 4. Strong responses at the  $m/z = 262$  and 264 ions, in approximately the expected 3:1 ratio, are obtained. The CID spectra for these parent ions, given in Figure 5, show approximately equivalent responses for the daughter ions  $\text{Cl}^-$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . The relatively strong responses for the  $\text{NO}_2^-$  and  $\text{NO}_3^-$  daughter ions are somewhat surprising, and suggest that the  $(\text{NG} \cdot \text{Cl})^-$  adduct bond has a strong covalent nature comparable to the strength of the C-O and N-O bonds of the nitrate functional group. It should also be noted that the formation of the  $\text{Cl}^-$  adduct of NG removes the MS response to a higher mass region where chemical interference will be less important; this could be emphasized by using bromoform as the chemical ionization reagent.

A number of volatiles were observed in the

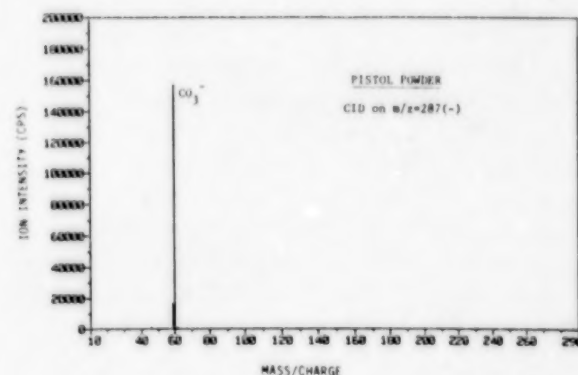
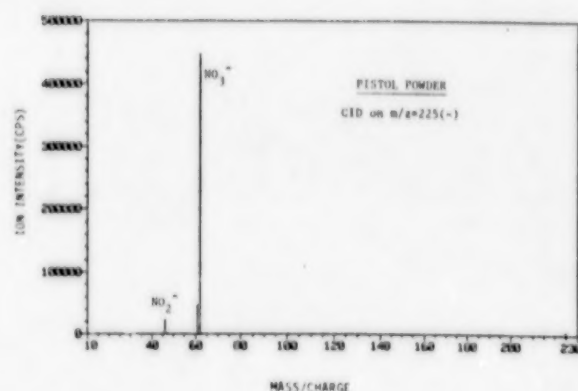
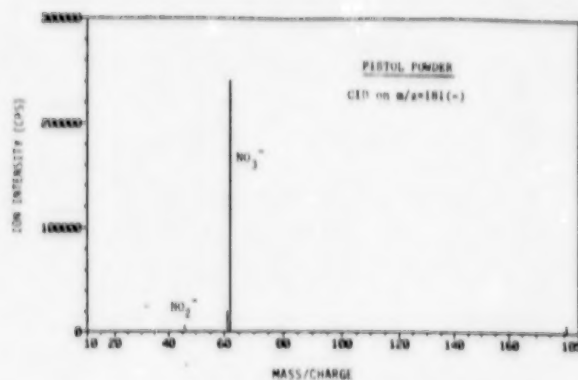


Figure 3. CID spectra of some of the parent ions observed upon ionization of the headspace vapors above double-base pistol powder.

headspace vapors above a sample of recrystallized TNT, as shown in Figure 6. The CID spectra of the  $m/z = 197$ , 226 and 227 ions are given in Figure 7. All show a prominent  $\text{NO}_2^-$  daughter ion. It can be concluded that the  $m/z = 227$  ion corresponds to  $\text{M}^-$ ,  $m/z = 226$  to  $(\text{M} - 1)^-$  (loss of a proton) and  $m/z = 197$  to  $(\text{M} - \text{NO})^-$  (probably due to nucleophilic substitution of reagent  $\text{O}^-$  for  $\text{NO}_2$ ).

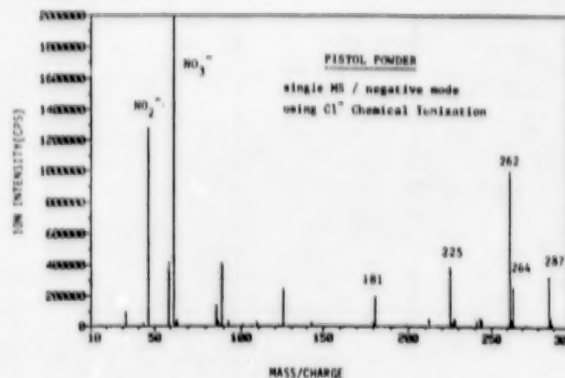


Figure 4. Single MS spectrum of the headspace volatiles above doublebase pistol powder using  $\text{CI}^-$  chemical ionization.

The headspace above RDX was examined under positive ionization. Several volatiles were observed (Figure 8), some of which may be useful for the detection of RDX. Of particular interest was the ion appearing at  $m/z = 223$ , which corresponds to the molecular weight of protonated RDX. In view of the extremely low volatility of RDX, it would be surprising to see this ion. This suspicion was confirmed by running the CID spectrum of the  $m/z = 223$  ion, which identified that ion as protonated diethylphthalate (a common plasticizer). This result emphasizes that false alarms may be triggered even given the specificity of mass spectrometry, but such false alarms can be avoided by using the enhanced specificity of MS/MS.

The TAGA system has been specifically designed for immediate (real-time) response to changes in the concentrations of trace vapors in ambient air. Figure 9 shows the real-time response (single MS mode) to samples of TNT, DNT and NG momentarily introduced near the inlet of the TAGA. The real-time MS/MS response to TNT, monitoring the formation of the  $\text{NO}_2^-$  daughter ion from the  $m/z = 227$  and 197 parent ions, is shown in Figure 10. As no attempt was made to heat-trace the sample inlet, some sample line memory is observed as a long "tail" after the sample was removed; in a real-life situation the sample line would be heated to eliminate this memory effect.

## CONCLUSION

The TAGA MS/MS system with Atmospheric Pressure Chemical Ionization permits the instantaneous detection of trace concentrations of explosives vapors in air. All of the explosives studied gave rise to a number of volatiles, some of which may be useful for the detection of explosives;

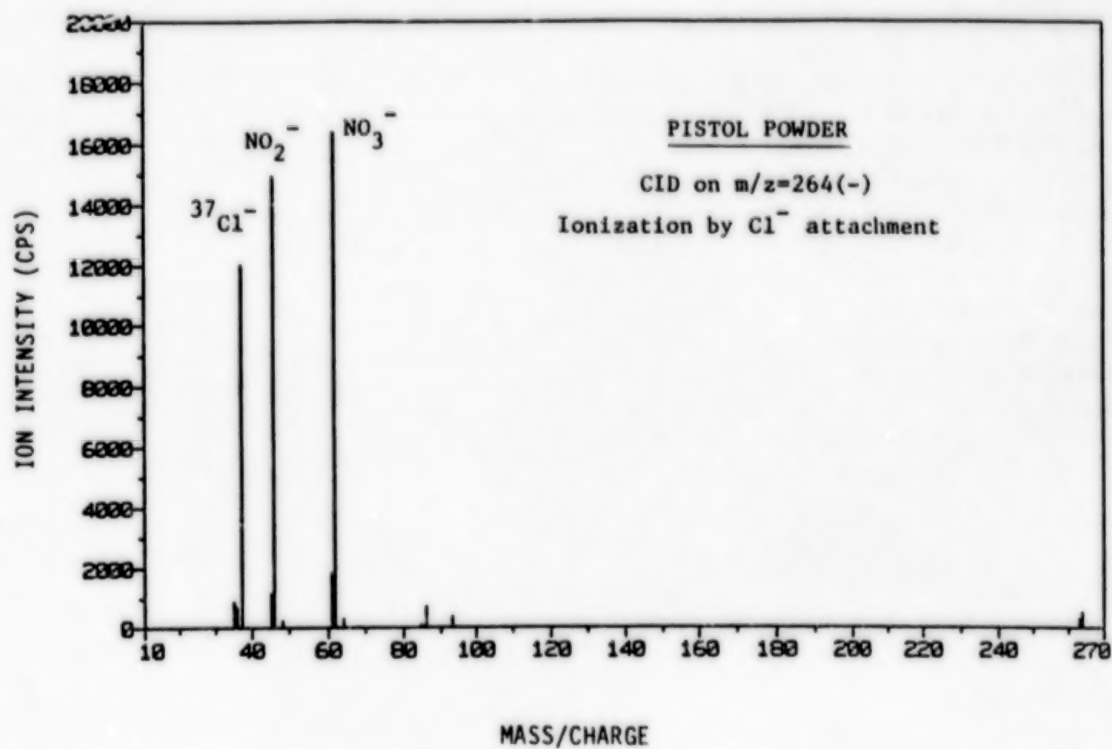
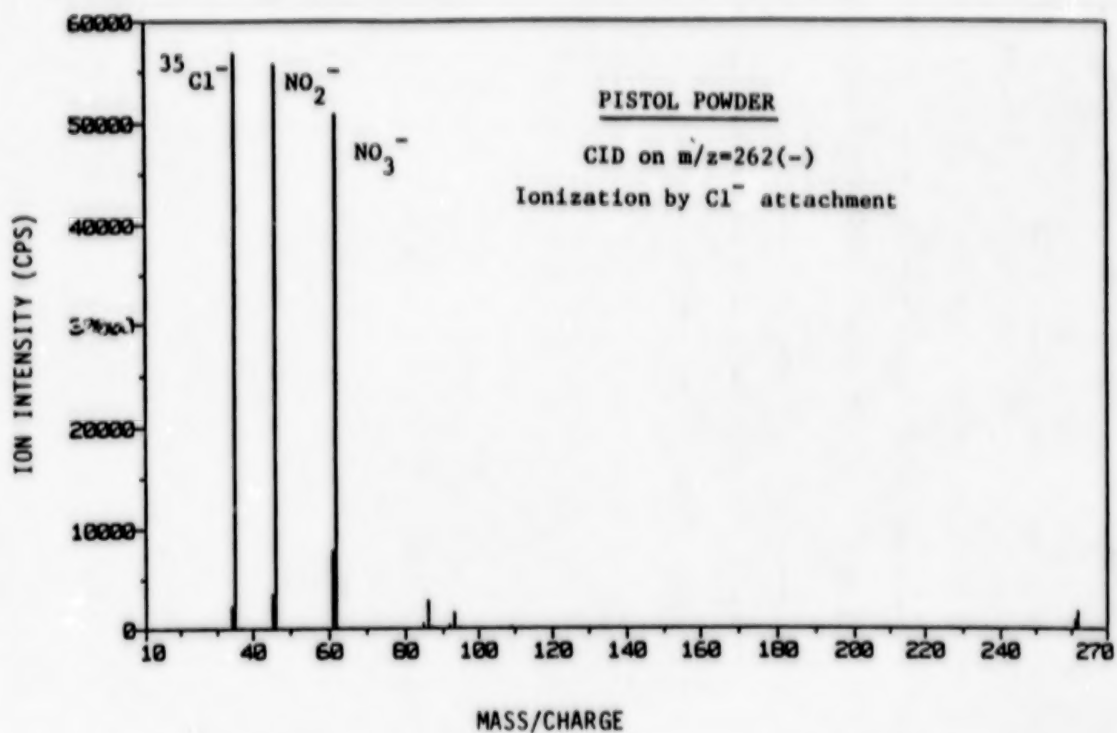


Figure 5. CID spectra of the chloride-adduct ions of NG.

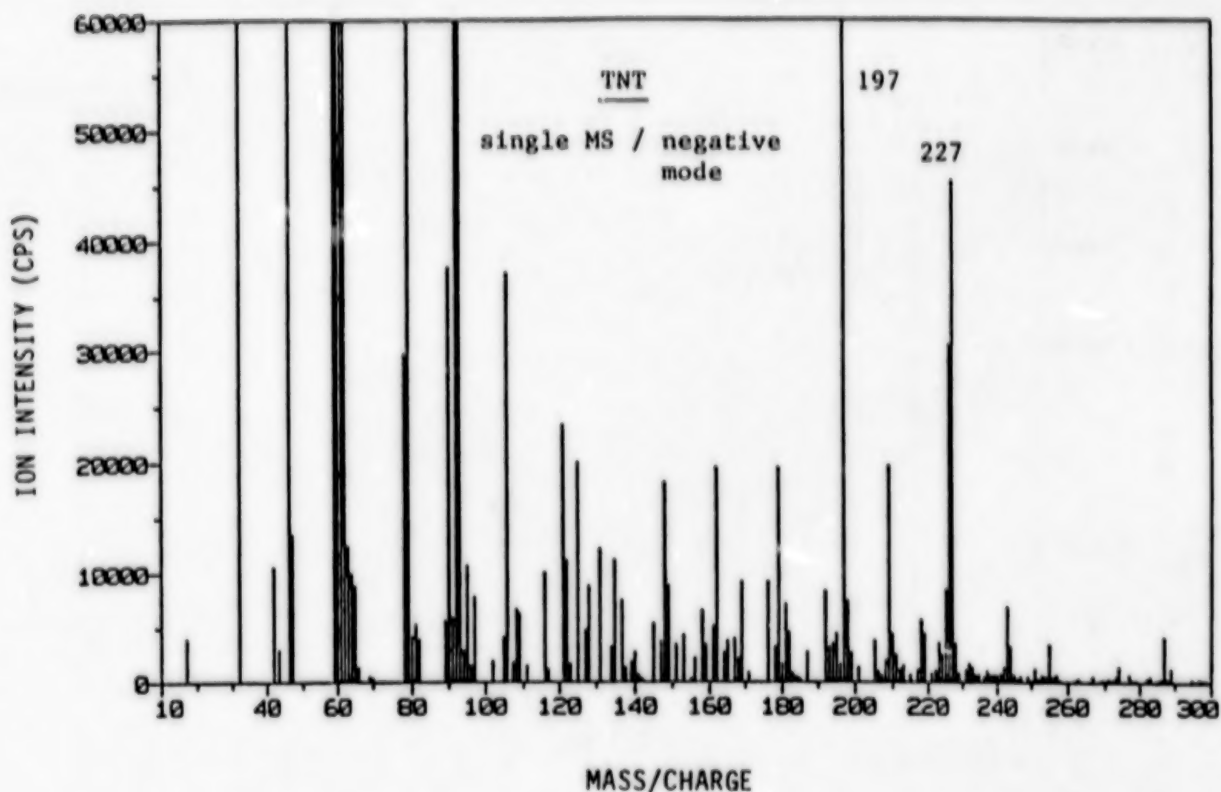


Figure 6. Single MS spectrum (negative mode) of the headspace volatiles above TNT.

more effort on the characterization of these concomitant vapors is warranted. Nitroglycerine is most sensitively detected in the negative ionization mode using  $\text{Cl}^-$  as the reagent ion to promote the formation of the halide-NG adduct ion. TNT may be detected readily as the  $\text{M}^-$  ion and as the  $\text{M} - \text{NO}^-$  ion. Collision Induced Dissociation of the nitrate-explosives (NG, EGDN) gives rise to prominent  $\text{NO}_3^-$  daughter ions, while the nitro-explosives (TNT, DNT) generate  $\text{NO}_2^-$  daughter ions. Caution is advised in the analysis of single MS results: the detection of diethylphthalate of  $m/z = 223$  could be confused with RDX

(which is isobaric, *i.e.* has the same nominal molecular weight), although MS/MS can readily distinguish the two.

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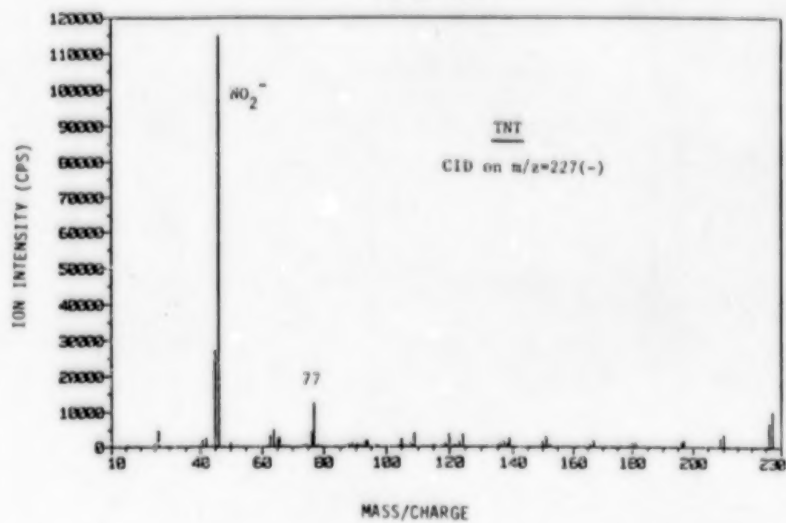
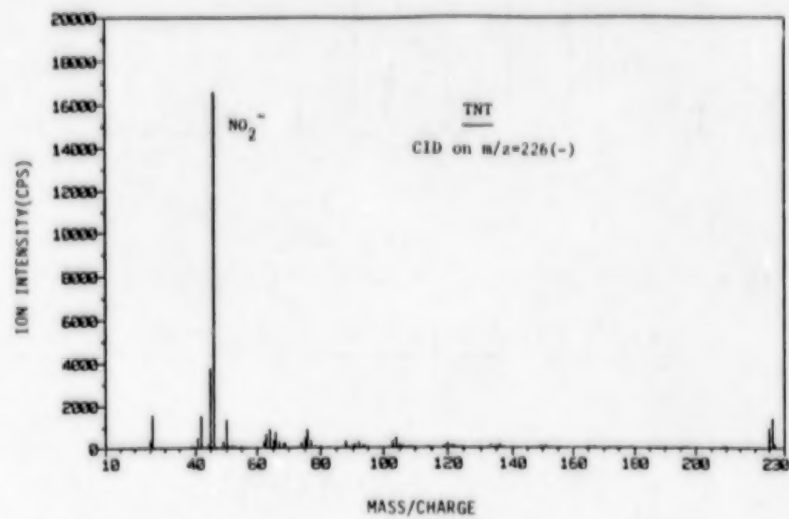
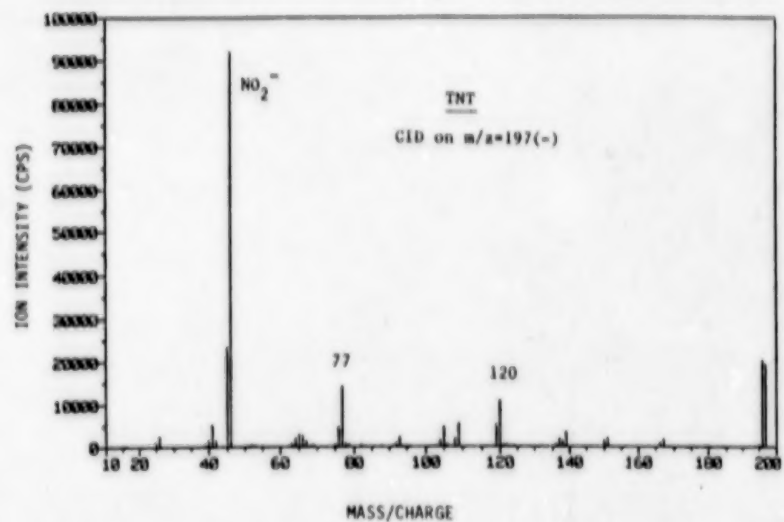


Figure 7. CID spectra of some of the parent ions observed upon ionization of the headspace vapors above TNT.



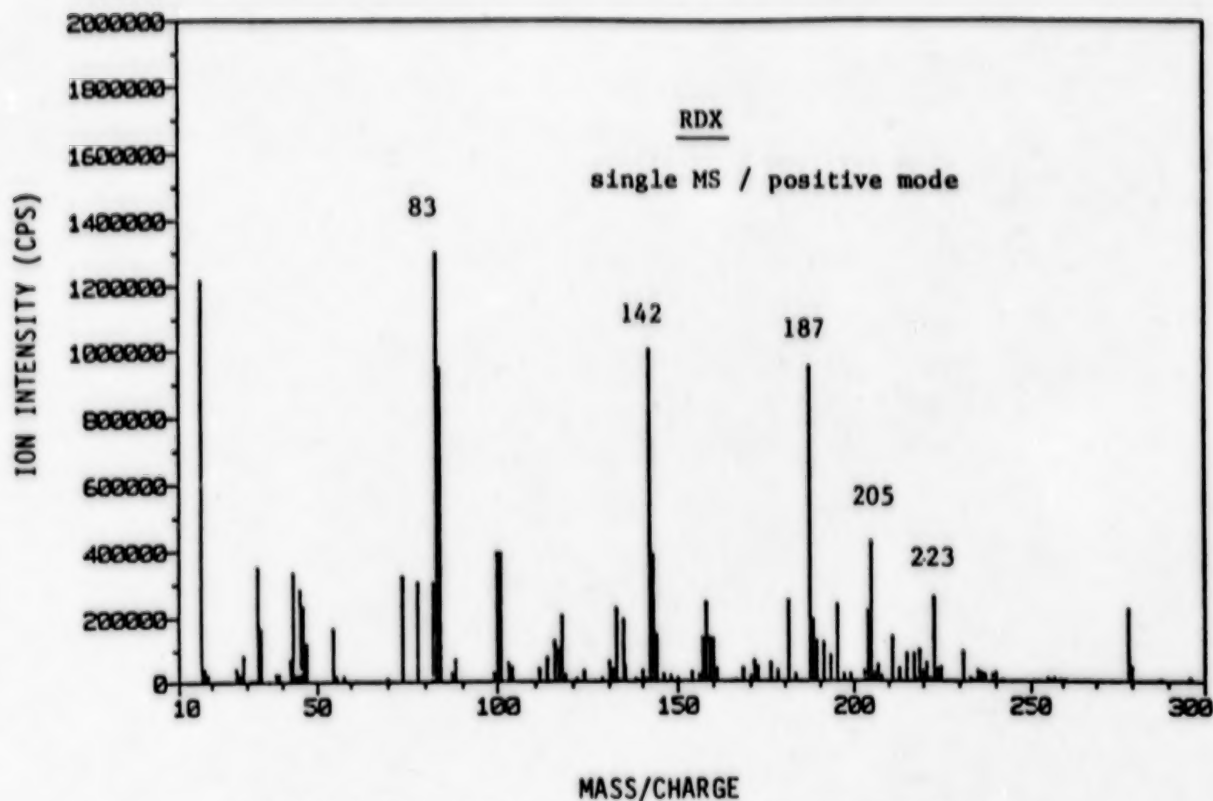


Figure 8. Single MS spectrum (positive mode) of the headspace vapors above RDX.

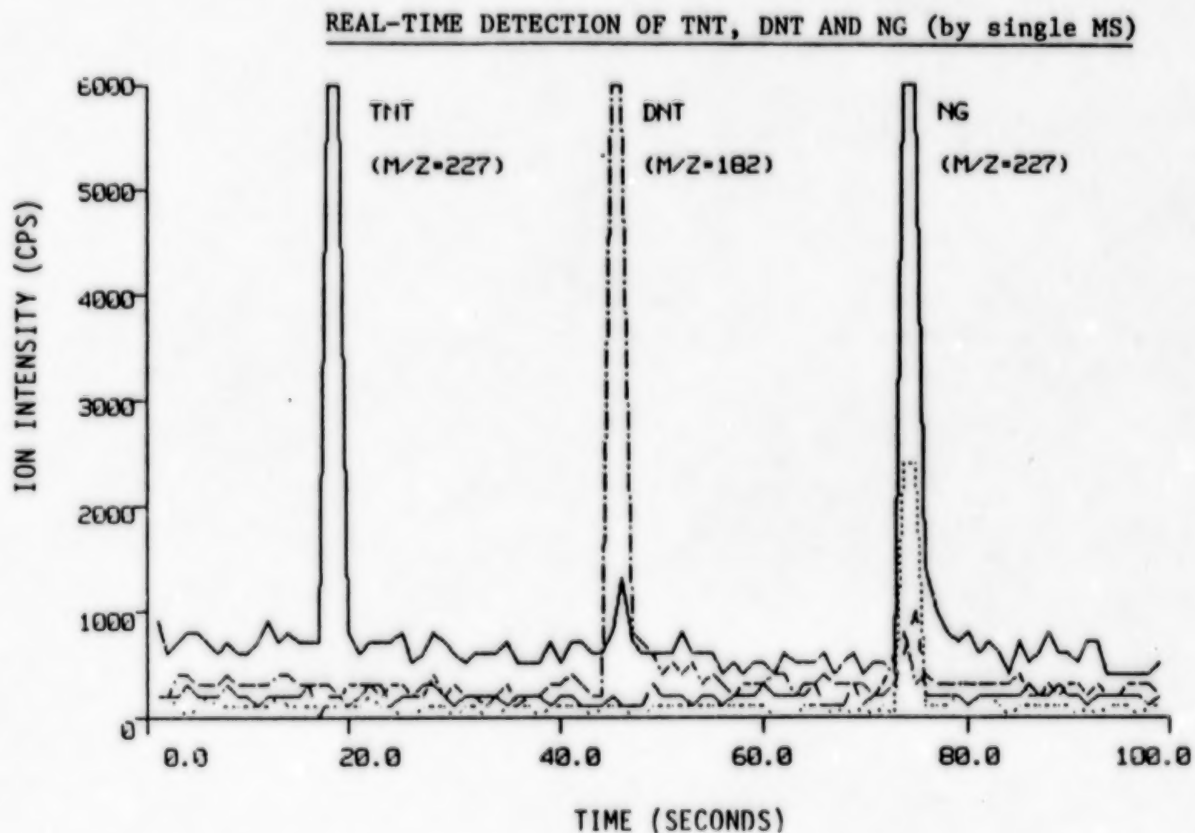


Figure 9. Real-time response (single MS) to TNT, DNT and NG.



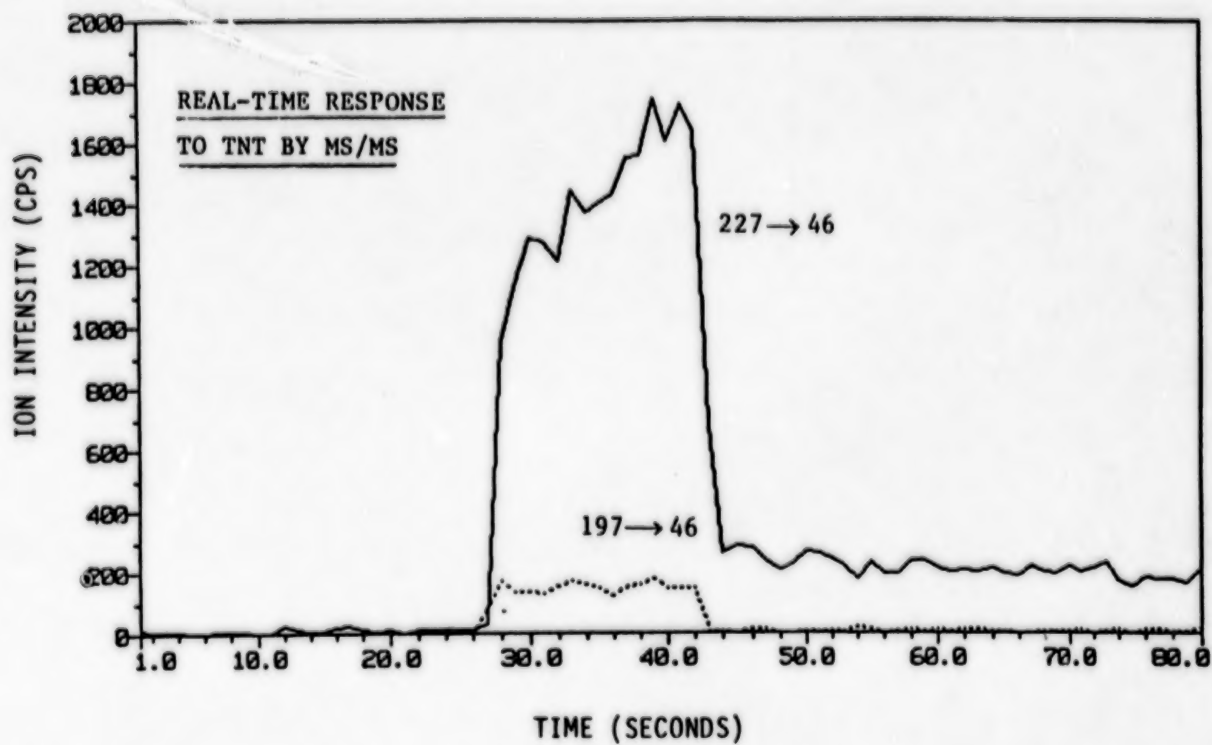


Figure 10. Real-time response to TNT by MS/MS.



## A MAN PORTABLE GCMS FOR EXPLOSIVES DETECTION

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**ABSTRACT.** A highly integrated design, light-weight and low power consumption gas chromatograph-mass spectrometer has been developed and successfully operated as part of the NASA Viking mission to the surface of Mars.<sup>1</sup> The rigorous criteria established by NASA for the Viking Mars Lander resulted in an instrument that was physically compact, highly shock resistant and capable of remote operation through a command and control linkage with data return to earth. The design of this instrument evolved over an eight year period of extensive analytical testing and refinement of system elements to meet the specifications established for remote planetary operations. The principal elements of the Viking GCMS are being re-packaged into a configuration suitable for terrestrial analytical applications ranging from environmental monitoring to a variety of forensic and security uses, including explosives detection. The result is a unique analytical tool that combines the power and sensitivity of a laboratory GCMS instrument in a small valise-sized, man-portable device that will allow field measurements and identification of unknown volatiles with maximum sensitivities of the order of 0.1 parts per billion (in air by volume). The essential design and operational characteristics of the Viking GCMS system will be highlighted in connection with explosives detection applications.

### INTRODUCTION

The combination of Gas Chromatography with Mass Spectrometry over 25 years ago<sup>2</sup> brought together these two powerful analytical tools to provide a new capability for organic analyses that has been applied to an increasingly diverse series of applications. The technique is perhaps most effective when complex organic mixtures are involved as well as with samples that are very dilute and quite often in the presence of contaminants or other masking compounds. Such conditions often confront the forensic scientist, with the result that numerous examples of GCMS use in this field have been reported.<sup>3</sup> A particularly important use is in analysis of explosives and high energy propellants, which has been discussed in a recent survey

of the field by Yinon and Zitrin (Pergamon Press, 1981). Mass spectra of explosives and explosive mixtures have been catalogued and variations in their characteristics under various forms of ionization schemes have also been investigated.<sup>4</sup>

For the most part, commercial GCMS systems have been intended for laboratory use, in which there is a highly controlled environment with little effective limitation on space or power requirements for the instrument. There are a variety of such systems commercially available, with very high sensitivity and recently, with mass ranges that are well above 1,000 amu. These units typically are designed to be flexible and permit different ionization approaches and sample handling techniques and frequently are teamed with a microprocessor

for automatic adjustment of electric potentials and other controllable variables. Sophisticated data handling and processing is provided with library search and signature recognition capability becoming available. A major improvement in computer-aided interpretation of unknown spectra using the probability-based matching (PBM) system has recently been reported<sup>5</sup> that will permit real-time, on-line identifications to be made during the GCMS run. Further improvements seem likely and alternative approaches to computer-aided compound identification are being pursued that have similar capabilities. In short, the techniques of GCMS analysis have been refined and are continuing to improve to provide even greater efficiency and versatility for a wide range of organic analyses.

While the laboratory use of GCMS has flourished, the development of field portable instruments with these capabilities has been very limited. One approach, taken by a Canadian firm, SCIEX, Inc., involved essentially moving a laboratory instrument, with some modifications into a large, mobile van.<sup>6</sup> This system, using the TAGA 3000 GCMS instrument, with atmospheric pressure chemical ionization, has been used for a variety of field environmental measurements where the Van and GCMS could be brought to the vicinity of the test site. Another approach that has been taken has been to miniaturize and ruggedize just the MS portion of the system, to produce a portable mass-analyzer that can be taken into the field with relative ease.

This paper will describe the development of a complete, man-portable GCMS, of high sensitivity, with simplified operational characteristics and proven performance.

### THE VIKING GCMS

In the early 1970's, the National Aeronautics and Space Administration was given approval for a series of two unmanned scientific missions to Mars, to orbit the planet at close range and to place two landers on the surface to perform scientific measurements including tests for the presence of life or complex organic substances that may be a precursor to life. The challenge facing NASA was to condense a carefully chosen set of instruments that would perform the required tests into a very compact and light-weight lander system capable of withstanding the rigors of heat-soak sterilization, launch vibrations and accelerations, then traverse interplanetary space for six months or so,

and after the shock of landing on Mars, function successfully millions of miles from earth, subject to cold surface temperatures and blowing dust.

A key instrument in the experiment package was a GCMS because of its flexibility and specificity in identifying unknown substances as well as its sensitivity. The development of the Viking GCMS was carried out at the Jet Propulsion Laboratory of the California Institute of Technology, supported by several major contractors and the Viking science team. A detailed description of the development of this instrument has been published<sup>8</sup> and the scientific results from its successful operation on the surface of Mars have been reported.<sup>9-14</sup> The current development of a terrestrial, man-portable GCMS is largely based upon the Viking instrument, the essential features of which will be summarized here.

The Viking GCMS can best be understood through reference to a systematic flow diagram, Figure 1. The instrument was designed to permit direct atmospheric sampling through a molecular leak, Valve 9 then Valve 12, for test of atmospheric constituents, after removal of carbon monoxide, carbon dioxide and water. For full GCMS testing, soil samples were collected, introduced into the sample processor, were pyrolyzed and the vapors were eluted with hydrogen as a carrier gas and introduced to the GC column. Downstream of the column is a five-stage effluent splitter (Valves 4, 4A, 5, 6, and Restrictors R5, 6, 7) which is controlled by the MS ion pump to prevent pump overload and maintain sample concentrations within the analyzing range of the MS. A palladium alloy separator is used to remove the hydrogen carrier gas, and the sample is introduced into the MS through V7.

The MS is a Nier-Johnson, 90° electric sector, 90° magnetic sector double-focussing instrument, electrically scanned, with a mass range of 12-215 amu. It uses an electron bombardment ion source with selectable ionizing energies of 45 and 70 eV, and a relatively slow scan rate of 10 sec. The ion pump for the MS uses the same magnet as the magnetic sector, with pumping speed for most gases of 500 cm<sup>3</sup>/sec. This design approach allowed a very compact MS assembly and kept instrument weight down.

The GC is a micropacked column, 2m long by 0.75mm I.D., packed with Tenax-GC, 60-80 mesh coated with 2 percent solution of Poly-MPE. The demonstrated performance of the Viking GCMS included a resolution of 200 (10 percent

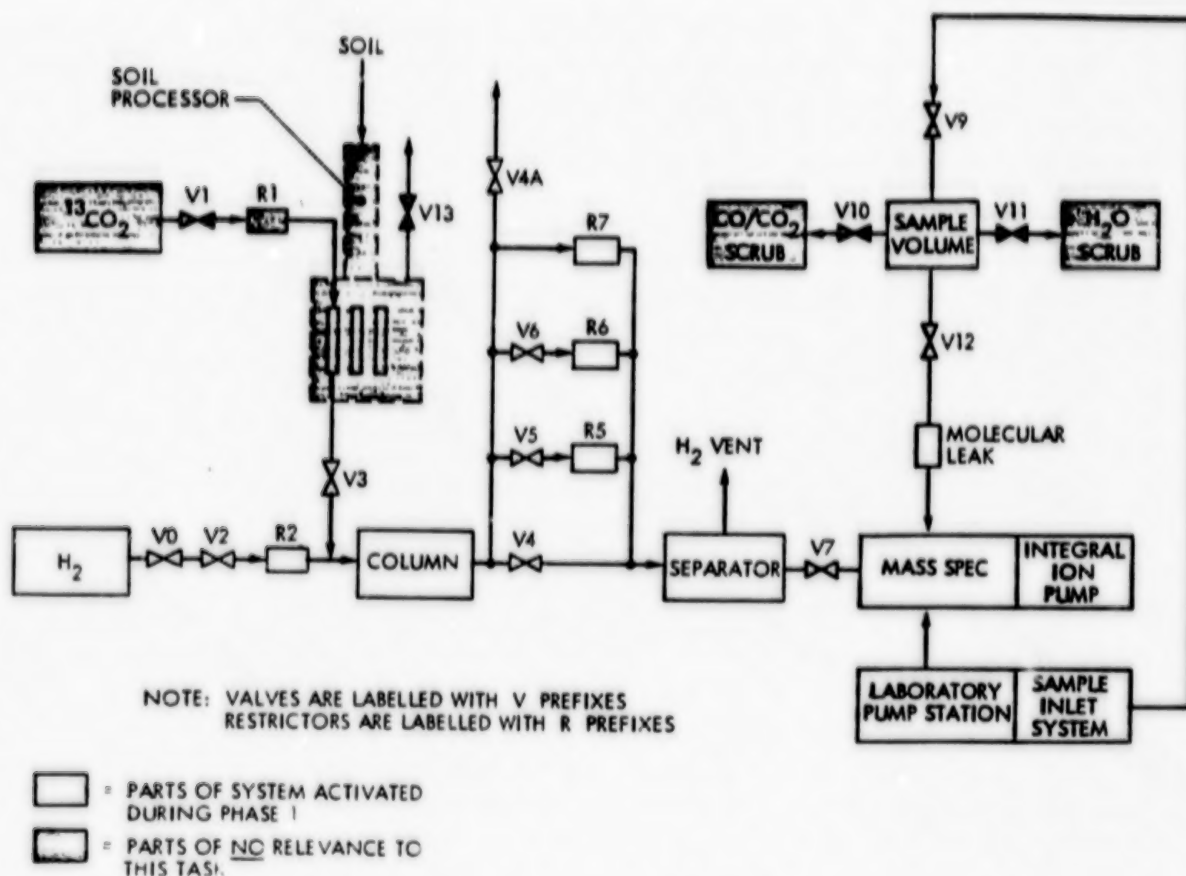


Figure 1. Viking GCMS flow diagram.

valley) at 200 amu with a detector sensitivity of  $1.7 \times 10^{-8}$  amps/ngm-sec. Figure 2 is a block diagram of the major subsystems and their relationships.

An important part of the design criteria for the Viking GCMS was to minimize both the weight and volume of the unit and reduce power requirements in order to reduce demands upon the Lander which was highly weight and power constrained. Another important characteristic is the resistance to shock and vibration that was required in order to space-qualify the instrument. Additionally, there was an obvious requirement for remote-control operation of the system which entailed special attention to interfaces, stability of operation, pre-programmed functions and sequencing, electrically operated precision valves, and a highly reliable data collection and relay system. All of these aspects of the Viking GCMS design make it particularly suitable for adaptation to a portable terrestrial instrument.

#### Terrestrial Adaptation

After the Viking Mars landing mission, there were two spare flight instruments that have been

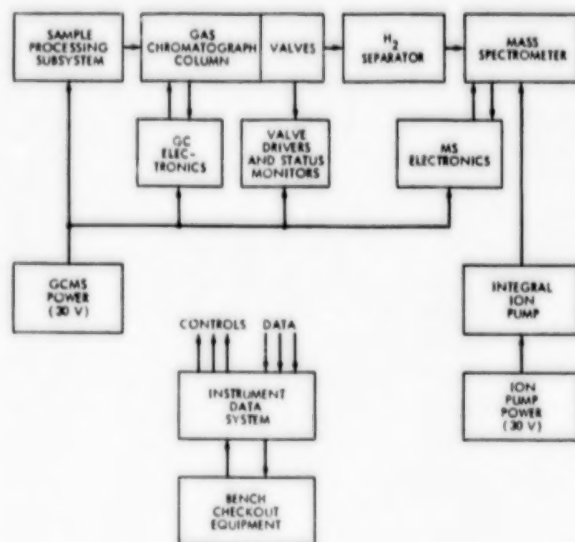


Figure 2. Flight configuration of the Viking GCMS.

kept under vacuum in a standby mode for six years. One of these instruments is being modified to establish the feasibility of a portable terrestrial GCMS system, suitable for a variety of in situ analytical applications.



The principal subsystems that require modification from the original Viking configuration are the GC column, the GC-MS interface and the scan rate and mass range of the MS. In addition, suitable methods of sample collection and introduction into the GCMS must be defined, depending upon the nature of the application.

Specific design criteria for these subsystems are reviewed in the following sections.

### Mass Spectrometer

The MS in the Viking instrument has a mass range of 12-215 amu. However, for most portable terrestrial applications a range of about 400 amu will be necessary to make adequate identification of many of the complex spectra that will be encountered. In the MS, the following relationship connects the Mass and the two major variables (magnetic field and ion accelerating voltage):

$$M = 4.8 \times 10^{-5} \frac{(RB)^2}{V}$$

where R = radius of curvature of the magnetic sector (cm)

B = magnetic flux density (gauss)

M = mass of the ion (amu)

In the existing instrument, R = 3.8cm, B = 6330 gauss, and V varies between 130 and 2330 volts. To focus higher masses on the detector, either the accelerating voltage or the magnetic field must be changed. If the accelerating voltage is lowered, however, the result will be an increase in velocity aberration and consequent loss of resolution as well as loss of sensitivity because of the greater number of ions that drift off the instrument axis. The alternate approach has been chosen, that is, an increase in magnetic flux density to 9000 gauss, which results in an accelerating voltage of 140 for mass 400. The velocity aberration will cause a slight decrease in resolution of the MS at the higher mass numbers. The scan time of the MS will be decreased from 10 sec. to 3 sec. to improve sample analysis.

### Interface Between the GC and MS

The Palladium-silver separator will be replaced by a two-stage membrane separator in order to avoid possible chemical reaction with the carrier gas, hydrogen, with palladium acting as the catalyst. This interaction would seriously affect PCB detections, for applications. The new interface will be connected to the GC column and will be heated simultaneously within the thermal zone to

eliminate the need for a separate heater. A silicone membrane is being investigated together with a simple cannister pump of sorptive material in the interstage region of the separator to aid in removing the carrier gas.

### Gas Chromatograph Column

A modern fused silica WCOT capillary GC column will replace the original Viking GC packed micro column. In order to shorten analysis time, which is especially important to a field portable instrument, the GC typically will operate in a manner that provides only sufficient separation to allow unambiguous identification and quantitation of samples by the MS while maintaining total analysis time within reasonable limits.

For many terrestrial applications, the effluent from the capillary GC column will be split, with one part sent to an electron capture detector (ECD) and one part to the MS through the separator membranes. The ECD will assist in monitoring the performance of the GC column.

### Auxiliary Subsystems

Sample introduction into the GCMS requires both a detailed understanding of the likely field environments to be encountered and the characteristics of the substances that are to be identified. Collection of vapor samples, if sample concentrations are high, may be made with a simple probe or, if relatively simple mixtures are present, via direct injection into the MS through a molecular leak. Most applications, however, require further sample processing before introduction into the GC or MS. In general, the sample collection subsystem will have a probe with a small pump to obtain adequate flow into the concentrator cartridge which will be thermally desorbed and directed either to the GC or directly to the MS depending upon the nature of the application being carried out. Other examples of the sample pre-processing are beyond the scope of this paper. A survey of typical methods for various explosives analyses may be found in the recent monograph by Yinon and Zitrin.<sup>15</sup>

A particularly important part of any modern GCMS is the data processing, storage, retrieval, and analysis subsystem. The Viking GCMS in its basic design is compatible with a high degree of automation and computer-aided data handling. Valve sequencing and operation of the system will be computer controlled as well as initial data handling. The resolved ion current analogue signal



(RIC) from the MS detector will be digitized and processed using a data processing system developed at JPL under the sponsorship of the National Institute of Health.<sup>16</sup> The fully portable system will include an on-board microprocessor system, capable of supporting fully automatic systems operation. Investigation of on-board signature analysis capability is in process, to complement the operating system control functions.

### EXPERIMENTAL PROGRAM

With these general directions established, the process of concept validation has been underway at the Jet Propulsion Laboratory, with a special emphasis upon the capability to test for organic vapors, such as PCBs or explosives. The performance objectives of this program are outlined in Table 1. This shows the specifications for a first

generation system which is a direct extrapolation of the Viking Mars Lander instrument as well as subsequent incremental improvements currently planned.

### Power

The power requirements for the proposed GCMS are not significantly different from the Mars Lander GCMS power requirements. A complete GCMS analysis on the Viking instrument lasting one hour would consume power at the rate of 80 watts. The instrument would therefore require 80 watt-hour of energy per analysis. The necessary power could be tapped from a domestic power line or from an internal power supply. In any event, a small battery would be required to maintain operation of the ion pumps which will consume 0.04 watts in the instrument standby mode.

Table 1

	"First Generation" Viking GCMS (System One)	Viking GCMS w/ Generic Magnetic Sector	Viking GCMS w/EOLD
Mass Range	a) 12-215 amu b) 24-430 amu	12-500 amu	Two ranges 12-78 amu 78-507 amu
Scan Rate	3 sec over mass range	3 seconds	Non scanning > 40 ms/range spec- tral integration time
Ionization Mode	EI 25 eV and 75 eV	EI 10-100 eV or Field Ionization	EI 10-100 eV or Field Ionization
Resolution	200 @ 200-400 amu 10% valley (entire mass range)	500 @ 500 amu 10% valley	500 @ 500 amu 10% valley
Size/Weight	21 Kg + battery weight *	TDB—This would determine ultimate specifications	25-30 Kg + battery weight *
Operating Mode	GCMS Direct MS Enriched MS	GCMS Direct MS Enriched MS	GCMS Direct MS Enriched MS
Mass Stability	$\pm 0.1$ amu	$\pm 0.1$ amu	$\pm 0.1$ amu
Detector Sensitivity	$2.5 \times 10^{-8}$ A/ng/sec $10^{-13}$ A- $10^{-6}$ A dynamic range	$2.5 \times 10^{-8}$ A/ng/sec $10^{-13}$ A- $10^{-6}$ A dynamic range	$10^{-15}$ gm detectability

\* 0.9 Kg per hour of operation

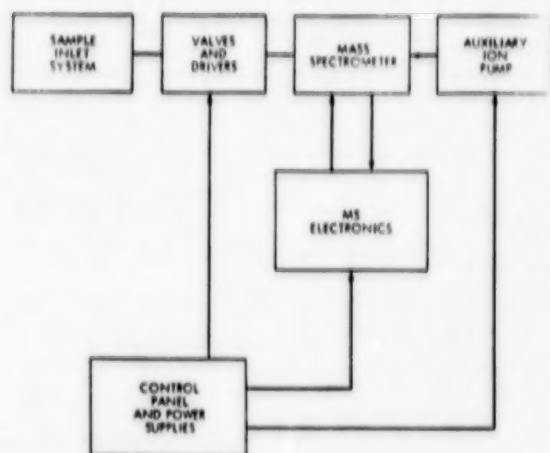


Figure 3. Laboratory test configuration of the mass spectrometer.

It is estimated that an on-board power supply (battery pack) would weigh approximately 0.9 kg per hour of operation.

#### Weight of the System

The existing Viking GCMS system weighs 18 kg including the electronics. Adding the necessary modifications such as a larger magnet, GC column, an appendage ion pump, a two stage membrane separator with its own intermediate stage pump, electronics, interface box, a sample extraction kit and an aluminum carrying case would increase the weight to about 27 to 29 kg.

Figure 3 shows the flow diagram of the mass analyzer, modified for validation testing. Using a modified Mars flight instrument shown in Figure 4, that had been quiescent for over six years, two test compounds were introduced into the MS system to demonstrate system operation, sensitivity and mass resolving power. To provide insurance that an adequate vacuum was maintained an auxiliary laboratory system was connected to the MS since control circuitry for RIC was not connected. This later proved to be redundant.

The two compounds chosen to illustrate MS operation were Octafluorocyclobutane ( $C_4F_8$ ) (molecular weight = 200 amu) and Octafluorobutene-2 ( $C_4F_6$ ) (molecular weight = 200). These two test samples were chosen because the ion fragments generated from electron impact ionization cover the full mass range of the instrument for one of them, and nearly the full mass range for the other.

The mass spectrum of octafluorocyclobutane ( $C_4F_8$ ) is shown in Figure 5A. The mass spectrum was as expected. The parent molecule is unstable

and the most intense fragment ion appears at  $C_3F_7^+$  or  $m/e = 131$ . Very little ion intensity should be seen at the parent mass ( $m/e = 200$ ), as was observed. The strong ion signals at masses 100, 69, and 31 were produced by the fragment ions  $C_2F_4^+$ ,  $CF_3^+$ , and  $CF^+$ , respectively. Some doubly charged ion peaks were observed, as expected.

Octafluorobutene-2, on the other hand, is a more stable molecule. Hence a strong molecular ion at  $m/e = 200$  was observed (See Figure 5B). The expected two most prominent peaks in the spectrum,  $m/e = 69$  ( $CF_3^+$ ) and  $m/e = 131$  ( $C_3F_7^+$ ) were seen as was  $(M-F)^+$  at  $m/e = 181$ . Doubly charged ions were also observed from this sample.

The sensitivities determined from these measurements are  $0.8 \times 10^{-8} \text{ A} - \text{ng}^{-1} - \text{s}^{-1}$  at the 131 amu base peak for octafluorobutene-2 and  $2.3 \times 10^{-8} \text{ A} - \text{ng}^{-1} - \text{s}^{-1}$  at the 100 amu base peak for octafluorocyclobutane. This is consistent with and comparable to the Viking design sensitivity of  $1.7 \times 10^{-8} \text{ A} - \text{ng}^{-1} - \text{s}^{-1}$  at 28 amu for nitrogen.

Mass resolving power measured at  $m/e = 100$  and 181 is approximately 180 by the 10 percent valley definition commonly used in organic mass spectrometry. This is slightly below the design value of 200 but was expected from the higher instrument pressure. The pressure was higher than designed because it was operated without the integral ion pump being activated. Scattering of the ion beams by gas in the spectrometer analyzer is the cause of this phenomenon.

#### FUTURE WORK

Preliminary results of the terrestrial adaptation of the Viking GCMS have been encouraging and the next steps toward a fully portable instrument are underway. A prototype configuration for such an instrument has been established and is shown in Figure 6. Clearly, the major hardware elements of the system are easily contained in a small brief-case sized package which also accommodates the supporting electronics, battery, carrier gas supply and sample concentrator subsystem. Not shown is auxiliary equipment that may be used in connection with the introduction of samples to the GCMS. Preparation of samples is expected to involve a separate kit that would differ in detail depending upon the specific applications to which the GCMS would be applied. In testing for explosives, for example, both a vapor inlet probe and pre-concentrator would be included as

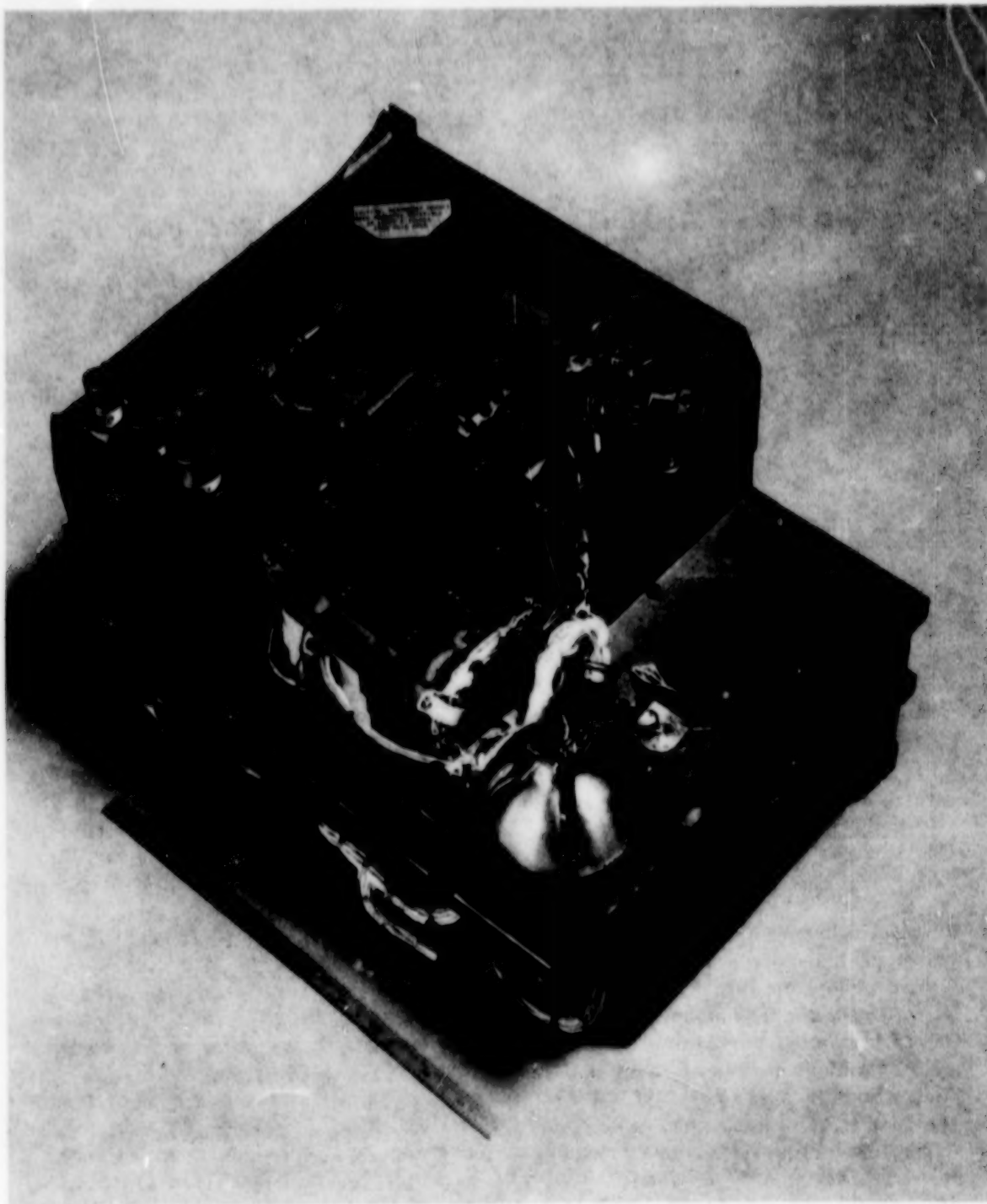


Figure 4.

well as elements that would permit various previously tested extraction techniques to be utilized.

Other uses would require a similar sample pre-processing kit but with different reagents.

Additional attention is being given to the control and display subsystems, including use of a flat plate programmable display unit that would fit

within the unit shown. With the successful demonstration of a fully adapted Viking GCMS system, versatile and sensitive laboratory-level GCMS performance will become available for truly portable analysis and field applications, which should be of value to a wide variety of explosives detection applications.

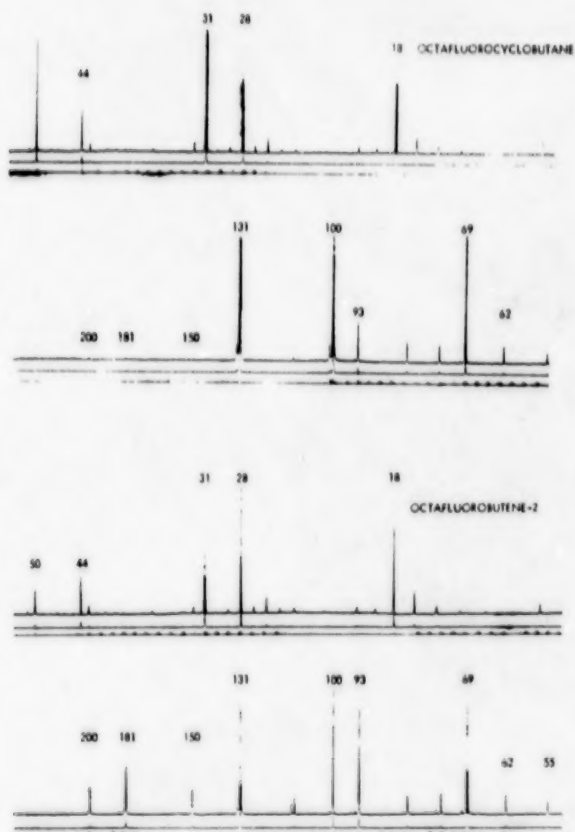


Figure 5A. Mass spectrum of octafluorocyclobutane obtained from the modified Viking mass spectrometer. 5B. Mass spectrum of octafluorobutene-2 obtained from the modified Viking mass spectrometer.

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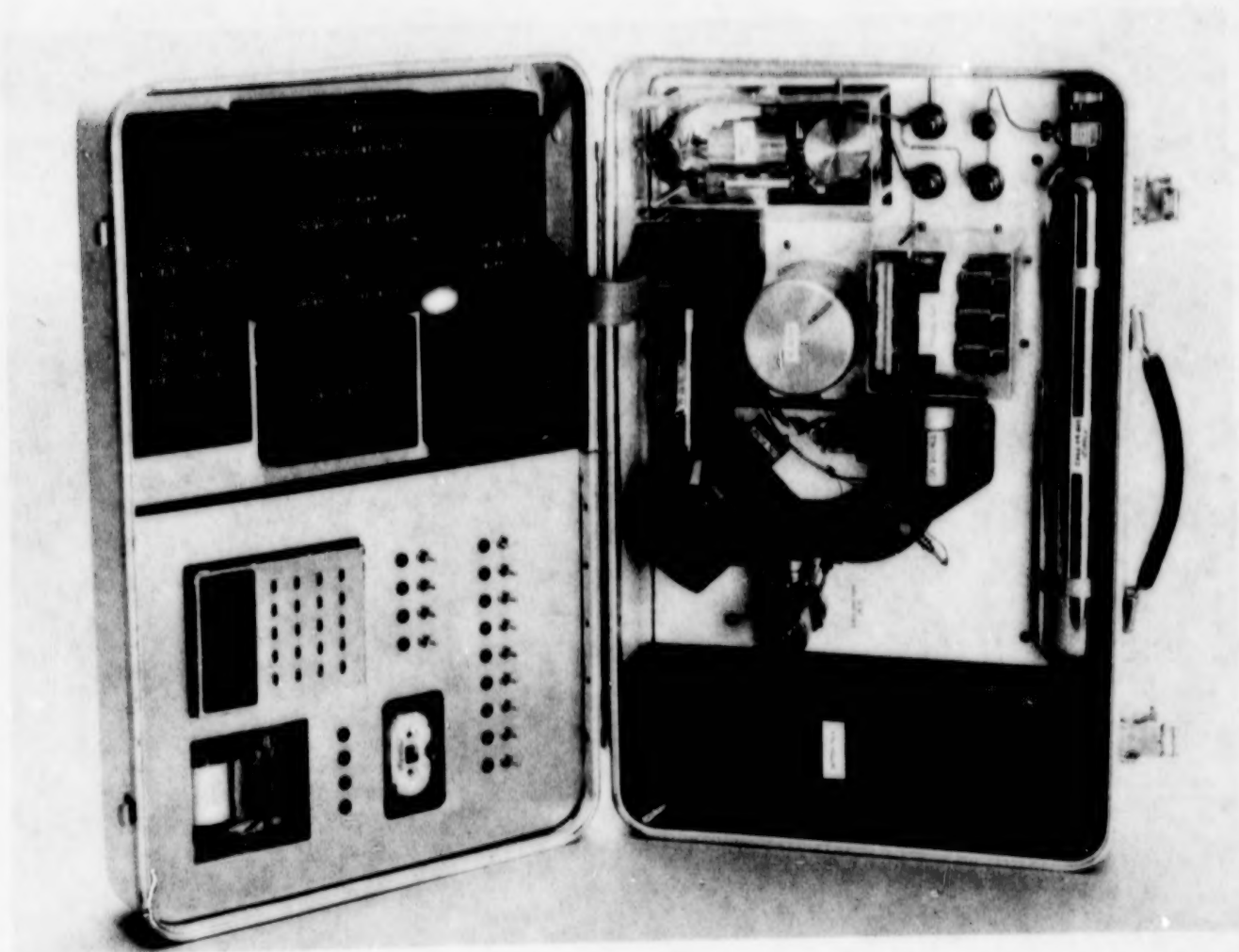


Figure 6.

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**TRACE VAPOR DETECTION  
OF HIDDEN EXPLOSIVES**

*Lorne Eilas*  
National Resource Council  
of Canada

**Paper No. 49 not submitted for publication.**



# **SAMPLING OF EXPLOSIVES WITH MULTIPLE, PORTABLE PRECONCENTRATING CARTRIDGES**

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**ABSTRACT.** A portable personal sampler has been developed to be used in searches for explosives. The personal sampler draws air through a cartridge where explosive vapors are preferentially absorbed on a treated filament. This preferential adsorption results in a preconcentration of explosive vapors. The cartridge is then removed and inserted into XonTech's Model GC-710 Explosive Detector where the cartridge filament is heated and the flashed off vapors are detected with an electron capture detector. Many commercial explosives, including TNT, C-4, dynamite, and detasheet, have been detected. Retention and sampling time curves for explosives show that detection is possible up to 30 minutes after sampling. The sampler is small (1.5 pounds) and relatively inexpensive. Several cartridges may be used with one sampler and several samplers may be used with one GC-710, thereby reducing the investment for search equipment.

## **INTRODUCTION**

XonTech, Inc. manufactures and sells the portable Model GC-710 Explosive Detector shown in Figure 1. While the GC-710 has been shown to be very effective in the detection of explosives, many of our prospective customers have asked if there is a less expensive way to conduct a search than for each searcher to carry a GC-710. The answer to this question is the subject of this paper which describes the use of the Model 7101 Personal Sampler.

The XonTech Model 7101 Personal Sampler is a small hand-held pump which draws air through a removable cartridge (Figure 2). The cartridge is interchangeable with the cartridge in the Model GC-710. Thus, a sample may be taken with a cartridge in the Personal Sampler, the cartridge removed, and the cartridge analyzed in the GC-710. The use of two to five Personal Samplers with three to five cartridges associated with each Personal Sampler would obviously allow more people to search using a single GC-710.

To evaluate the performance of the Personal Sampler, tests were run to determine its applicabil-

ity to an actual search. The efficiency of adsorption, the length of sample time, the dependence on flowrates, and the time between sampling and detection are described.

## **EXPERIMENTAL**

A XonTech Model GC-710 was used for all of the analyses presented in the paper. The GC-710 is a gas chromatograph containing a 10" x 1/8" O.D. FEP column of OV-275 on 40-60 mesh Chromosorb WAW. The oven temperature was isothermal and was set between 90 and 125° C in order to separate the explosive from the air peak. The detector is a direct current ECD using tritium (~150 mCi). The carrier gas is helium at a flowrate of 250 cc/min. Sample injection was made using a XonTech patented valve and cartridge (U.S. Patent 4,128,008). The cartridge contains a platinum filament which is treated with a chromatographic stationary phase (Figure 3). This chemical coating acts as a preconcentrator to remove the explosives from the air. Air is drawn over the filament at 300 to 500 cc/min. The absorbed explosive is injected into the GC by pneumatically inserting the car-

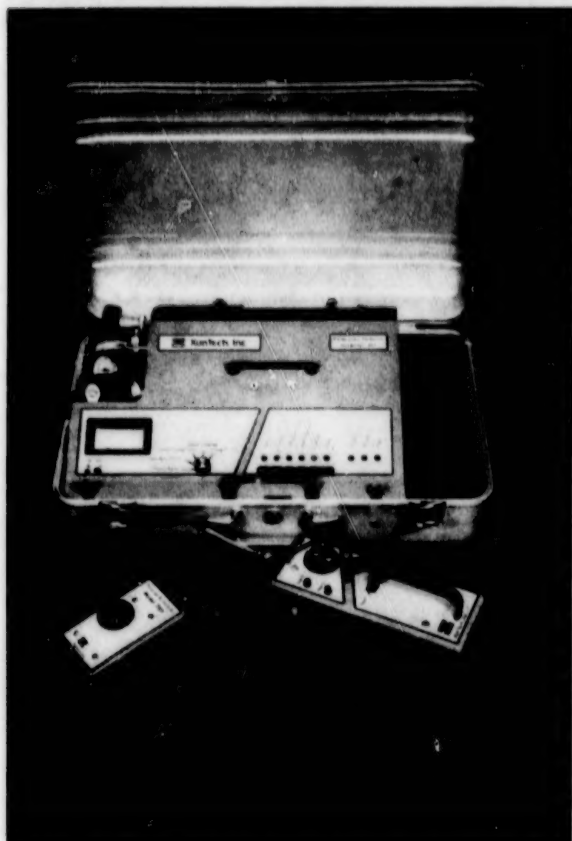


Figure 1. The XonTech Model GC-710 Explosive Detector and Model 7101 Personal Sampler.

tridge into the helium carrier gas stream. The explosive is released when the filament is heated.

This thermal release of explosives probably results in their decomposition. The result is that a large number of explosives give a substance which elutes within 6 to 9 seconds after injection. Independent evaluations have shown that many explosives elute a peak during the alarm window of the GC-710. These data are summarized in Table 1.

A XonTech Model 7101 Personal Sampler was



Figure 2. XonTech Model 7101 Personal Sampler with Sampling Cartridge and Battery Charger.

modified so that its pump was removed and it could be attached directly to the GC-710. This procedure allowed two cartridges to be tested in series. The efficiency of the upstream cartridge could be measured using this configuration (Figure 4-5).

The direct injection of samples into the GC-710 was used to determine the flow dependence of the cartridge.

Explosive vapor samples were introduced into a cartridge from two sources: Vials containing a small quantity of explosives and the XonTech Model 900 Calibrator. The calibrator is a Pella (1976) type and contains two ovens. In the first oven the explosive is maintained at a constant temperature so that the explosive will have an equilibrium vapor pressure. A small stream (0-50 cc/min) of inert gas sweeps the vapors into a second oven where the sample is diluted with 0-15 liters of air (see Figure 6). This oven prevents the explosive from sticking to the dilution plumbing.

In the calibrator, approximately 2 grams of dynamite was suspended on 20 g of Chromosorb G. This material was packed into a 48" x 1/4" O.D. FEP column. The column was cooled to 7° C and a flowrate 0.5 cc/min of nitrogen was passed through the column. The second oven was maintained at 40° C.

The explosives used were all from commercial sources in the Los Angeles area. Since we did not know the composition of the explosives no attempt was made to calculate a concentration. Concentration data presented below represent a 1/flow dependence.

Because the C-4, detasheet, and TNT samples were taken from vials, a purge of air equal to or greater than the sample flowrate was continuously passed through the vial so that the concentration was constant. The concentration depended upon the permeation rate of explosive out of the sample divided by the flowrate.

## RESULTS

The response of the GC-710 to the dynamite emitted from the vapor calibrator is shown in Figure 7. Over the range of interest the data were linear. These data confirm that as the concentration increases the cartridge will concentrate the explosive proportionately.

There was some concern that the cartridge filament surface area was very small and therefore only a small fraction of the explosive could be retained on the cartridges. On the contrary, it was

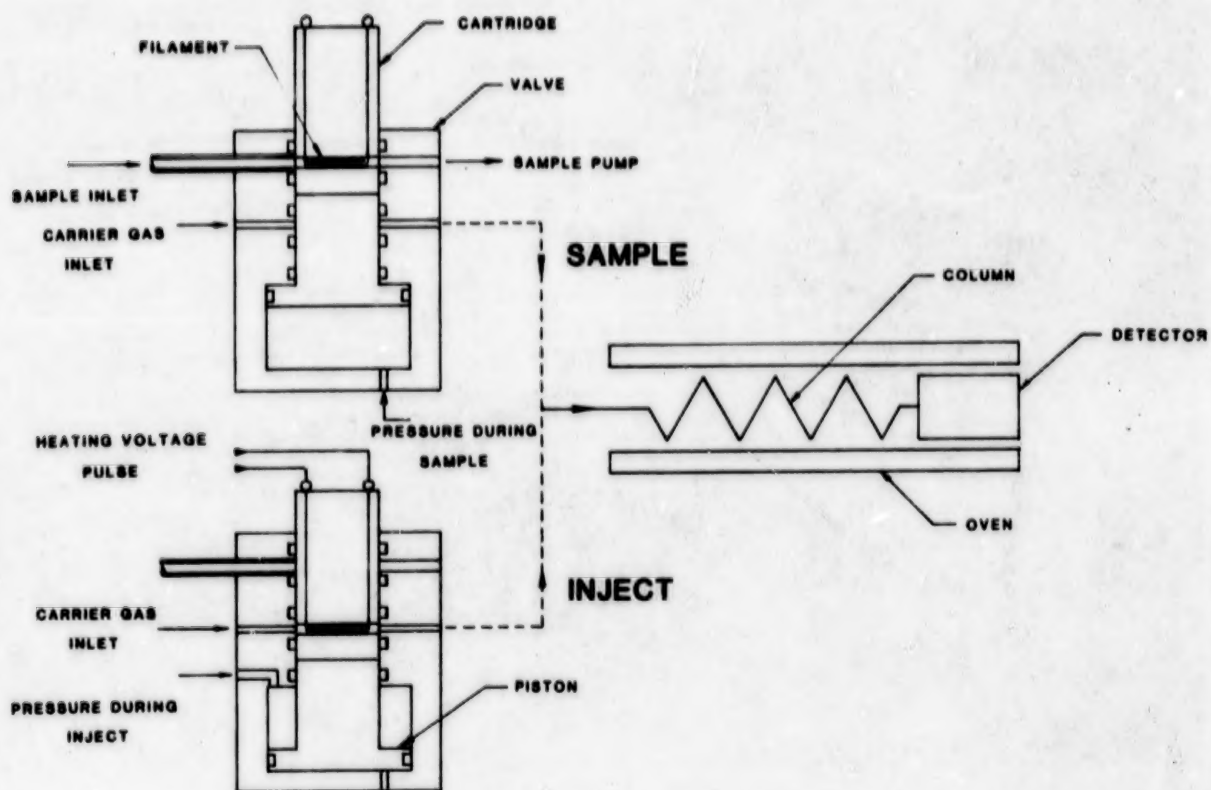


Figure 3. Preconcentrator Valve for the GC-710.

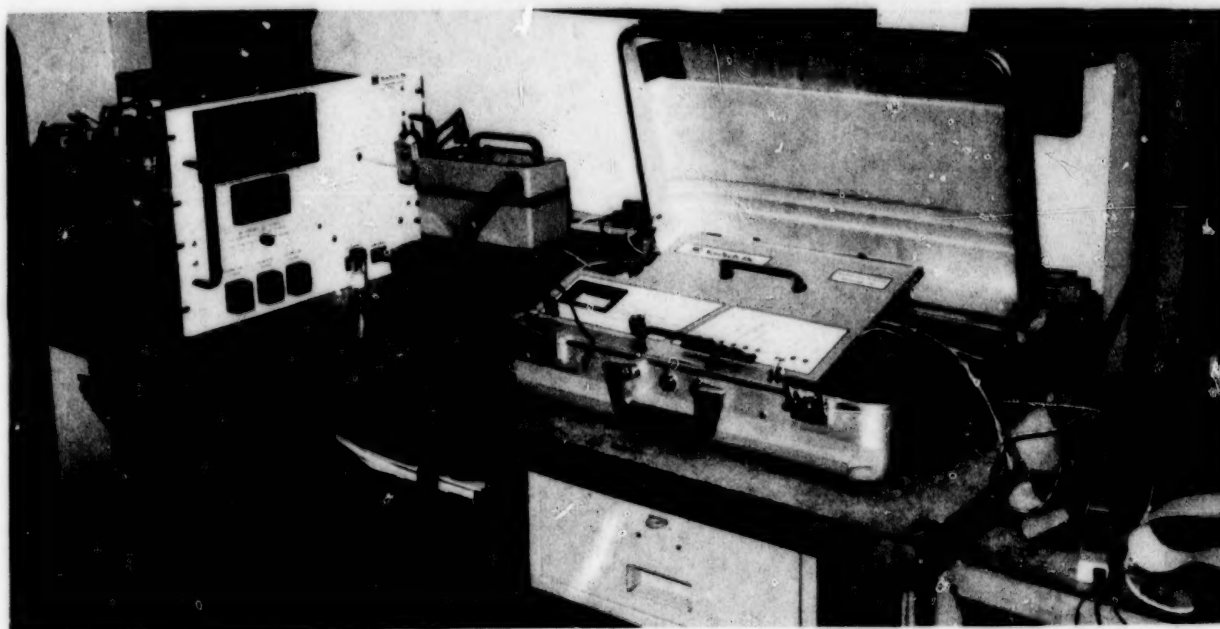


Figure 4. Experimental setup to check efficiency of sampling cartridge of the Personal Sampler with the GC-710 Explosives Detector.



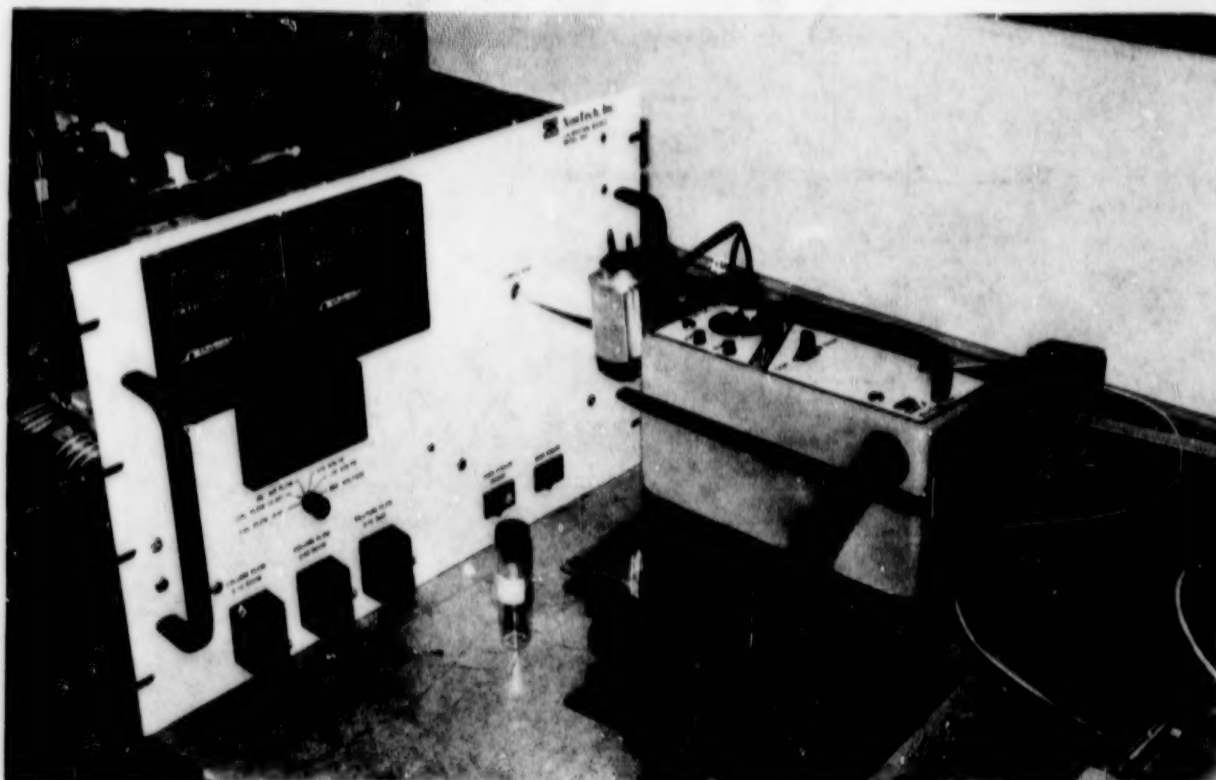


Figure 5. Experimental setup showing two cartridges in series and the XonTech Model 900 Vapor Calibrator.

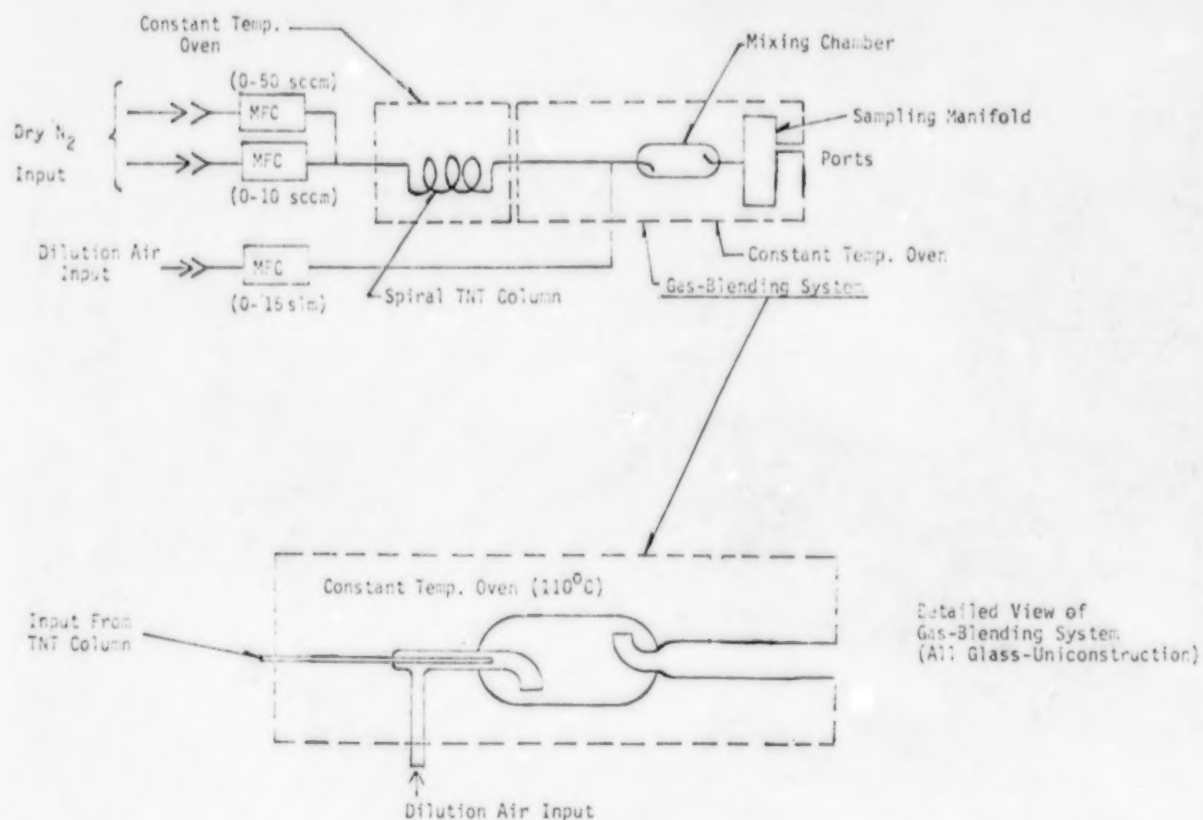


Figure 6. Flow diagram of TNT calibration unit.



**Table 1. XONTECH GC-710 RESULTS OF LABORATORY EVALUATION RESPONSES TO EXPLOSIVES AND PROPELLANTS**

Materials	Source	Response (1)	Response (2)
<i>Explosive</i>			
Composition C-4	Naval EOD (Old)		+ Alarm
Composition C-4	14th EOD		+ Alarm
Composition C-4	USPO		+ Alarm
Composition C-4	ATF		+ Alarm
Composition C-4	Naval EOD (New)		+ Alarm
Composition C-4	Picatinny Arsenal Std		No Alarm
C-4	USPO	S	
Composition B	Picatinny Arsenal Std		+ Alarm
Composition C-3	14th EOD		No Alarm
Swiss sheet	USPO		+ Alarm
Detasheet, C-3	14th EOD	S	
40% Dynamite	James D. Shea Co.		+ Alarm
Dynamite		ES	
Detonation Cord (PETN)	14th EOD		+ Alarm
PETN	Picatinny Arsenal Std		+ Alarm
PETN	ATF		+ Alarm
PETN		LS	
PBX9404		S	
Black Powder		LS	
Pistol Powder		S	
Rifle Powder		LS	
Black Powder	Sports Store		No Alarm
Dupont PB SB propellant	James Shea Co.		No Alarm
Dupont 4350 SB propellant	Sports Store		+ Alarm
Dupont 4320 SB propellant	Sports Store		+ Alarm
Dupont 4064 SB propellant	Sports Store		+ Alarm
Dupont 3031 SB propellant	Sports Store		+ Alarm
Hercules HiVel No. 2	Sports Store		+ Alarm
DB propellant			
Dupont 4198 SB propellant	Sports Store		+ Alarm
Dupont 4227 SB propellant	Sports Store		+ Alarm
Hercules 2400 DB	Sports Store		+ Alarm
propellant			
Hercules Unique DB	Sports Store		+ Alarm
propellant			
Hercules Bullseye DB	Sports Store		+ Alarm
propellant			
RDX, Type A <sup>d</sup>		S	
RDX, Type B <sup>d</sup>		S	
RDX	U.S. Army		+ Alarm
RDX	Picatinny Arsenal Std		No Alarm
HMX	Picatinny Arsenal Std		+ Alarm
Pentolite 50/50	Picatinny Arsenal Std		+ Alarm
Tetryl	Picatinny Arsenal Std		+ Alarm
2,4-DNT		HS	
2,4-DNT	Eastman Kodak		+ Alarm
TNT, Recrystallized		S	
TNT <sup>a</sup> , Flake		HS	
TNT <sup>a</sup> , Powder		S	
TNT	Eastman Kodak		No Alarm
TNT	U.S. Army 14th EOD		No Alarm
TNT	James Cline (TSC)		No Alarm
TNT	Hydronautics, Inc.		+ Alarm
Meta-dinitrobenzene	—		No Alarm
Para-nitrotoluene	—		No Alarm
Dupont Tovex Water gel	James Shea Co.		+ Alarm.

Materials	Source	Response (1)	Response (2)
Hercules Gel Powder A-2	James Shea Co.		+ Alarm
Water gel			
Trojan Trogel W-S-7	James Shea Co.		+ Alarm
Water gel			
Atlas NCN Aqua flow	James Shea Co.		+ Alarm
Water gel			
Sodium Nitrate	Mallinkrodt Chem.		No Alarm
Monoethanolamine Nitrate	Hercules Chem. Company		No Alarm
Methylamine Nitrate	Dupont		No Alarm
Ammonium Nitrate	Matheson, Coleman, Bell		No Alarm
Ammonium Nitrate		NR	
Diphenylamine-1	NAVAL EOD		No Alarm
Diphenylamine-2	NAVAL EOD		No Alarm
Diphenylamine	Mallinkrodt Chem. Company		No Alarm
Ethylcentralite-1	NAVAL EOD		No Alarm
Ethylcentralite-2	NAVAL EOD		No Alarm
<i>Inflammables</i>			
Diesel Fuel		NR	
Kerosene		NR	
Unleaded Gasoline		NR	
Acetone			No Alarm
Gasoline			No Alarm
No. 2 Diesel Fuel			No Alarm
Methyl Ethyl Ketone			No Alarm
Nitrobenzene			No Alarm
<i>Nonexplosives</i>			
Aftershave		NR	
Antiperspirant		NR	
Carbon tetrachloride		NR	
Fertilizer <sup>b</sup>		NR	
Preshave		NR	
Shoe polish		NR	
Smoke, cigarette		NR	
Snopake <sup>c</sup>		NR	
Snopake Solvent <sup>c</sup>		NR	
Zerex Antifreeze		NR	
Jaurellue Perfume			No Alarm
Fabulous Perfume			No Alarm
Old Spice After Shave			No Alarm
Trichloroethylene			No Alarm
Carbon Tetrachloride			No Alarm
S. S. Pierce Lavender Refresher			No Alarm
Exhaled cigarette smoke blown into inlet			No Alarm
Burning cigarette held at inlet			+ Alarm

\* Abbreviations: ES, extreme sensitivity; HS, high sensitivity; S, sensitivity; LS, low sensitivity; NR, no response.

<sup>a</sup> It is most likely the DNT content of these samples cause an alarm.

<sup>b</sup> Fertilizer mixture: N = 12%, Fe = 3%, S = 8%, phosphoric acid = 6%, potash = 4%, balance is inert filler.

<sup>c</sup> Contains large quantities of perchloroethylene.

<sup>d</sup> These samples contain a trace of TNT.

(1) Chapter 6 "Entry Control System Handbook", Sandia National Labs, June 1980

(2) Hobbs, John, "Evaluation of XonTech (Xonics) GC-710 Explosives Detector" FAA, DOT, Cambridge, Mass (1981)

found that sufficient explosive could be collected on the cartridge to completely remove all of the standing current when the explosive alarm peak eluted from the column.

Tests were conducted to determine the adsorption coefficient of the cartridge. The adsorption coefficient of the cartridge,  $P_i$ , is defined as

$$P_f = \frac{R_2}{R_1} \quad (1)$$

Where  $R_1$  is the response of GC-710 using an uncoated cartridge and  $R_2$  is the response of the GC-710 using an activated cartridge. The coated cartridge is reactivated by placing it in the GC-710 and heating the filament. Experimentally, the adsorption coefficient was determined by placing a coated activated cartridge between the source of explosives and the GC-710 as shown in Figure 5. When the sample was drawn through the activated cartridge the results compared with those obtained using an uncoated cartridge (filament of platinum was not chemically coated), the results shown in Table 2 were obtained.

To demonstrate the dependence of sample time on the retention of various explosives picked up by the cartridge, samples were taken for different sample times at a constant sample flowrate from a source of explosives at a constant concentration. These data are shown in Figure 8.

Sampling a constant concentration of dynamite at various flowrates showed an increase to the instrument response at the higher flowrates. The data in Figure 9 reflect these data. The GC-710 Explosive Detector samples at  $\sim 350$  cc/min. These data indicate that while both the Explosive Detector and Personal Sampler sensitivities may be increased by increasing the flowrate, restrictions due to weight and battery power presently limit this flowrate.

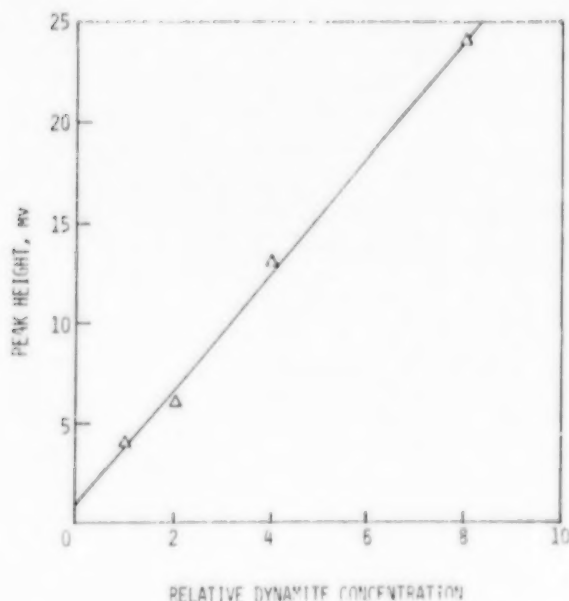


Figure 7. GC-710 response as a function of dynamite concentration. Sample flow is 330 CCM for 10 sec.

Table 2. ADSORPTION COEFFICIENTS FOR VARIOUS EXPLOSIVES ON GC-710 CARTRIDGE

Explosive	Adsorption Coefficient
DYNAMITE	0.64
C-4	0.45
DETASHEET	0.44
TNT	0.45

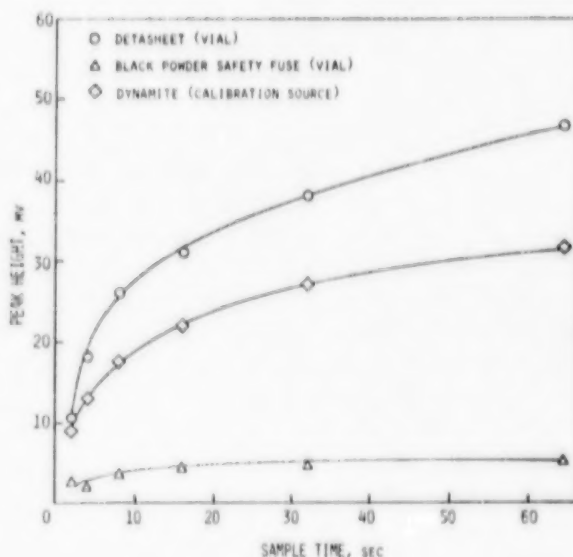


Figure 8. Response of GC-710 to various sample flow times. Sample flow is 330 ccm.

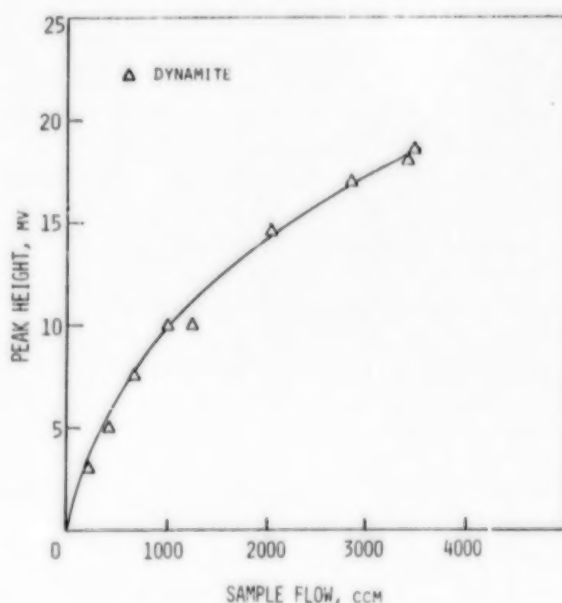


Figure 9. Response of GC-710 to various sample flows for a constant source of explosive.

When sampling with the Personal Sampler, care must be taken to prevent contamination of the unused or previously sampled cartridges and the potential loss of the explosive sample. For this reason XonTech recommends that each cartridge be placed in an inert cartridge holder whenever the cartridge is not in the instrument. Figure 10 shows four of these cartridge holders attached to a clip board.

With the use of these holders it was found that loss of explosives due to a waiting period between sampling and analysis was reduced. Waiting periods up to 30 minutes can be tolerated, as shown in Table 3.

The actual sampling time was investigated to see if the time an explosive was found during a search made any significant difference in the results. Assuming a searcher would use the sampler for one minute (sample pump runs for an integrated sample time of one minute), a test was made to determine if there was any difference due to sampling the explosive during any 10-second period of the one minute sample time. These data are shown in Figure 11. The results show little difference due to the sampling time.

These tests were repeated for dynamite over a two minute integrated sampling period. It was found that the response was significantly reduced by the additional minute of sample time.

### APPLICATIONS

In actual applications the Model 7101 Personal Sampler may be carried easily by a searcher to systematically search an area or room. For such a search XonTech recommends that two to five Personal Samplers be used with four (4) or five (5) cartridges. Figure 10 shows a search in progress. As the searcher proceeds around a room he/she would fill out a search record similar to one shown in Figure 12. The record shows what was searched with each cartridge. To preclude an excessive signal due to sampling a source of explosive for up to one minute, or the loss of signal due to excessive sampling time, XonTech recommends the use of a

**Table 3. LOSS OF EXPLOSIVE DUE TO WAITING AFTER A SAMPLE IS TAKEN.**

Waiting Time, min	Response on GC-710	
	Dynamite	C-4
1	5	2.5
5	4	
10	4	
30	4	2.2



Figure 10. Explosive search with Personal Sampler and four cartridges attached to clipboard with notes for search record.

maximum one minute integrated sample time for each cartridge when using the Personal Sampler.

Upon completion of the sampling, the clipboard with cartridges is returned to the instrument technician who examines each cartridge in the GC-710. The examination reactivates the cartridge so that it may be re-used. The searcher merely exchanges clipboards and continues to search. Figure 13 shows an exchange being made.

The instrument technician fills out an Explosive Analysis Record (Figure 14) for each analysis.

**Table 4. IMPACT OF PERSONAL SAMPLER**

	1 GC-710 Unit	5 GC-710 Units	1 GC-710 Unit w/5 Personal Samplers and 20 Cartridges
Weight, Pounds	43	215	50
Approx. Cost (\$)	10,000	50,000	18,000
No. of Searchers	1	5	5
No. of People Required	1	5	6

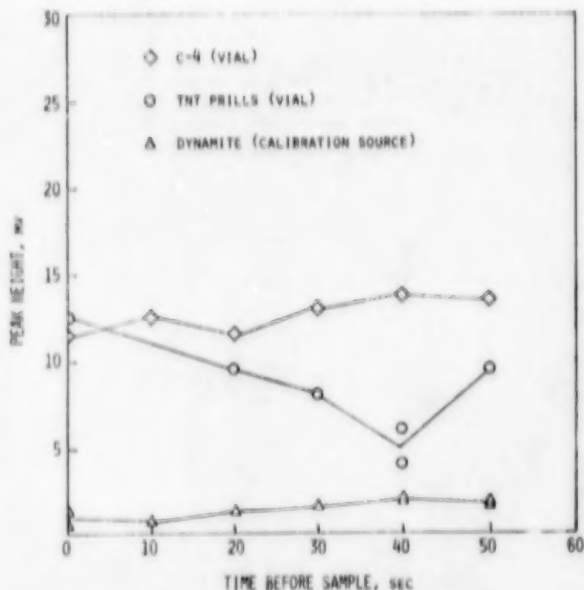


Figure 11. Response of Personal Sampler to a 10 sec exposure of various explosives at varying times during a 60 sec sample.



Figure 13. Exchange of samples and analysis of cartridges with XonTech GC-710 Explosive Detector.

EXPLOSIVE  
SEARCH RECORD

Facility Pentagon Date Feb. 2, 1983  
Room 316

Search clockwise around the room (left to right) after you check air ducts.

Cartridge No.      Search Areas

1.      Input airduct, Exhaust airduct, False ceiling,  
         4 chairs, pictures on wall.
2.      Book case, 3 plants,  
         small table
3.      Desk, desk chair,  
         wastebasket
4.      Credenza, briefcase,  
         file cabinet,  
         small book case

Unusual Packages \_\_\_\_\_

Searcher \_\_\_\_\_

Figure 12. Explosives Search Record.

Any unusual results can be noted for a request for an additional search.

The GC-710 can analyze one sample every 15 seconds. Thus, five searchers using four cartridges each can keep the GC-710 busy.

Facility Pentagon Date Feb. 2, 1983

Room	Cartridge	Alarm	Meter Indication
317	1	No	None
317	2	No	None
317	3	No	None
317	4	No	None
316	1	No	off scale
316	2	No	None
316	3		
316	4		

Operator \_\_\_\_\_

Figure 14. Explosive analysis record.

Another application for a Personal Sampler may be to search personnel who cause an alarm to occur in a walk-through screening portal. Figure 15 shows a person entering the XonTech Model 712 Personnel Explosives Screening Portal. Figure 16 shows him being searched with the Personal Sampler after the screening portal has alarmed.





Figure 15. XonTech Model 712 Personnel Explosive Screening Portal.

### CONCLUSIONS

The state-of-the-art of explosive detection using the GC-710 Explosive Detector allows the detection of most organo-nitrate compounds. The Personal Sampler makes possible the easy portability, collection, and preconcentration of explosives in a search device. The data presented here shows that a large area can be checked by the use of multiple cartridges and multiple Personal Samplers. The impact of the sampling of explosives



Figure 16. Personnel search after an alarm on the Personnel Explosive Screening Portal.

with multiple, portable preconcentrating cartridges is shown in Table 4. The cost reduction and weight reduction is a factor 3 and 4 respectively.

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## REMOTE DETECTION OF EXPLOSIVES USING TRAINED CANINES

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**ABSTRACT.** Through investigative research, Allied-General Nuclear Services, operating under contract to the U.S. Department of Energy, has developed a facility and technique for the remote detection of explosives. This work generally involved the remote searching of personnel entering sensitive areas of a facility. The work was generic in nature and the results can be applied to any situation where the carrying of explosives on personnel constitutes a threat. In that this system utilizes a remote detection concept, it does not violate individual civil liberties. The developed system involves placing the search subject in a booth and circulating a volume of filtered and air-conditioned air across and around the subject. The booth air is also recycled to assure proper mixing and minimum dilution. The booth air is exhausted and a sample of the air stream extracted by way of an isokinetic sampler. This sample of air is investigated by a trained canine in an area divorced from the search subject. Trained canine response indicates the presence or absence of explosive odors. While a number of explosives have been investigated using this remote detection concept, Commercial Dynamite and C-4 were used in full testing. Results showed nearly 100% detection and an error rate of less than 2%. Testing was conducted using small concealable samples of two to four ounces. Processing time during testing was twenty to thirty seconds per four-person group. Through ancillary tests, certain limitations of canine use in explosive detection were revealed. These involved odor concentration and discrimination problems. Methods of minimizing and overcoming these problems have been addressed and will be discussed.

### REMOTE DETECTION OF EXPLOSIVES USING TRAINED CANINES

For the past five years or so, at its Barnwell Nuclear Fuel Plant, Allied-General Nuclear Services has been doing some very interesting work in the area of Nuclear Material Safeguards under contract to the U.S. Department of Energy. "Safeguards," for those of you who may not be familiar with the term, is a two-sided function somewhat peculiar to the nuclear industry. One side is involved in the monitoring of Special Nuclear Material (plutonium or highly enriched uranium) in a processing facility and accounting for this material. The other side of Safeguards is the Physical Protection of the facility itself and the Special Nuclear Material within it. The physical threats protected against are *sabotage* (those acts which would disable the facility and/or cause

radiation to be released, thereby posing a danger to the general public), *theft* of Special Nuclear Material (the overt or covert theft of large quantities of material by insiders and/or outsiders), and *diversion* of Special Nuclear Material (the theft of small quantities of material usually by an insider and usually over a long period of time).

I would like to discuss with you today the work we have done in one area on the Physical Protection side of Safeguards, dealing with the threat of sabotage in particular. Most acts of sabotage involve the use of explosives. As part of the control of personnel access to sensitive areas of a nuclear facility, operators of such facilities have the responsibility to assure that explosives and other incendiaries do not enter these areas. Large quantities are not of great concern because visual inspections will generally reveal attempts to carry these

large quantities through an access control point. What is of concern, however, is the carrying-in of small, concealable quantities which could be cached inside, and later gathered and formed into a device that could cause significant damage.

Our mission was to develop a system of searching personnel for small amounts of explosives with a high degree of accuracy in a cost-effective and expeditious manner. There are, of course, several alternative methods available to approach this mission. One alternative was to conduct universal or sporadic "pat-down" searches of employees. This was fairly quickly discounted for two primary reasons. First, to provide for expeditious movement of personnel especially during a shift change, a large number of both male and female security personnel are required for "pat-down" searches. This is both costly and presents security manpower scheduling/use problems. Secondly, and more importantly, the use of physical "pat-down" searches could be construed by employees as a personal affront which would present serious Employee Relations problems.

Another alternative is the use of explosive detection instruments using electron-capture technology or the more recently developed gas-chromatography instruments. These devices are currently in use at many nuclear facilities but their use is subject to some reservations by operators and regulatory agencies alike. The reservations are the high cost of these instruments and the low probability of detection on some explosive compounds (like C-4 and Black Powder). Another concern is the time factor necessary to assure an acceptable probability of detection level. The hand-held units appear to be more accurate than the walk-through portal units, but are more expensive and slower. Therefore, more units and personnel are required to process large numbers of personnel expeditiously.

In our work, we studied a search method combining a system of accuracy (high probability of detection), speed of search (a goal of less than 30 seconds per employee), and cost. In that canines had a long history in bomb detection work, we first investigated work done by others. This led us predominantly to the U.S. Air Force, Sandia Labs/Southwest Research Laboratory, U.S. Customs, and several European law enforcement agencies. We found that the canine olfactory system had great potential for our application. Additionally, the canine possessed other attributes that made it even more attractive. A dog is portable

and therefore could be used in various locations. He adapts well to environmental change (inside/outside). He is capable of many tasks beyond explosive detection and therefore potentially had more "use time" which increased his cost effectiveness. The canine also had some drawbacks, of course. He requires initial training, reinforcement-training, care, and maintenance. The canine presented another potential problem—that of employee problems and civil liberties problems if the dog was exposed directly to employees. But, overall, it appeared to us that when properly managed, the dog represented a potentially valuable and cost effective tool. We felt that the Employee Relations and civil liberties problems could be precluded through proper design and management.

After investigation, we concluded that the canine could be used for explosive screening of personnel and many other things, but that it was imperative that the dog be in a position remote from employees and employee traffic. The problem then became: "Keep the dog away from the people and somehow transport the scent from the employee at physical point 'A' to the canine at remote physical point 'B.' "

There ensued a very interesting evolution of design, training, and behavioral study. For this discussion I shall concentrate primarily on facility design.

Our first attempt was what we now fondly call "the closet portal." In this phase of our work, we placed the dog and handler in a "closet" with a floor which was five feet by six feet. The search subject stood in a verticle "telephone booth"-like affair which was affixed to the outside of the "closet" door (Figure 1). The search subject "box" had air holes placed in such a manner that air would be drawn across all parts of the search subjects body, and passed through the "closet door" via a four-inch diameter "scent port" approximately 20 inches above floor level. The "air-handling" equipment was a variable speed drum blower with a maximum of 350 scfm mounted on the rear wall of the "closet" and exhausting air out of the closet. The air flow pattern then was from the room, through the "telephone booth," through the "scent-port," and finally through the "closet" and out the wall to the outside. This arrangement had one very serious flaw in design: the confinement of the "closet" did not permit the dog to move while working, which, we found most dogs prefer to do. Moreover, the close confines of the "closet"

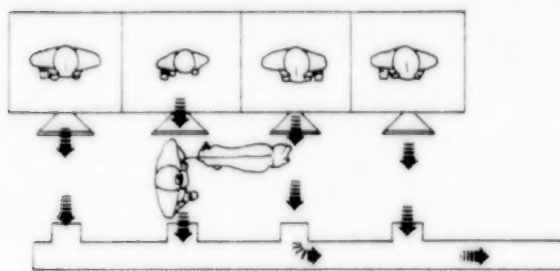


**The Closet**

Figure 1.

caused the animal, out of courtesy I am sure, to occupy the least space possible—which is a sitting position. This unfortunately coincided with his “alert” position—which is also sitting. It was somewhat obvious, however, that the dog was detecting the explosive odors when present and, of course, when his attention was directed to his work. Therefore, we concluded that the theory held promise, but the facility design was almost totally inappropriate.

From the “closet,” we advanced to the first real set of booths. We constructed four booths of heavy plywood and coated them with an epoxy paint inside and out. The booths were approximately three feet square and seven feet high inside



**First Booths**

Figure 2.

(Figure 2). The epoxy coating was recommended by Sandia Laboratories and provided us with a very cleanable surface from which to remove residual explosive odor. The booths had locking doors with a sealing medium to prevent air from leaking out of the booth. Air was supplied from the variable speed blower mounted on top of each booth. The air was taken from the room, blown down upon the search subject and back out into the room through a “scent-port” located at the back side of the booth and approximately 20 inches above floor level. The “ports” were covered with wire mesh to “protect” the search subject from the canine. Behind the row of booths was an area 5 feet wide and 20 feet long. This provided adequate room for dog and handler to work. In a short time, the routine for searching each scent-port was established with the canine. We started with positive and negative plants placed about one foot off the floor of the booth. Fairly quickly, we had indications of much improved detection rates. They were on the order of 85 to 90% and a 10 to 15% false alert rate. Then we introduced people into the booths in sets of four. The detection rates went down and the false alert rates went up.

To summarize this test phase, we found the following:

(a) The dog was falsely alerting on food, cosmetics, and other unknown personal odors. This was later eliminated by a period of avoidance training.

(b) We believe that the reduced detection level was also caused by longer test periods and a resultant buildup of explosive vapors in the room due to exhausting the booth air into the room and recycling that air back through the booth. As a temporary remedy to this, we set a large fan at the back door of the room and pulled air through the opened front door. This helped but did not totally solve this problem.

(c) We found that we were getting a very laminar flow of air from the blower-port down across the subject which tended to hamper a “whole booth” sample of air. A subject could hold the sample near a wall and we would miss it. We tried several diffuser designs at the inlet port and this helped. We also installed “whisper fans” on two opposite inside corners of the booth pointed 45 degrees to the wall and 45 degrees to the floor. The whisper fans and the mixing of air they provided aided considerably in bringing the detection rate up.



(d) We found that air velocity at the scent port was most critical. If it was too low, there was not enough vapor for the dog to sample. If the velocity at the scent port was too high, it seemed to disturb the dog's whiskers to a point where he would actually avoid the scent port due to the discomfort. Additionally, high velocity tended to dilute the explosive vapors thus reducing probability of detection. We briefly tested the system using air flows ranging from 0.6 scfm to 30 scfm. We found a composite "comfort range" and "minimum odor dilution level" to be 7 to 9 scfm.

(e) We found that lingering or residual odor was a problem for it usually resulted in a false alert on the next pass. Extensive "flushing" of the booth with air is essential in reducing or eliminating this problem. The flushing time necessary is a function of the size of the booth, the finish on the booth walls, the type of explosive and, of course, the amount of air passing through the booth. In the booths described in this phase, we found that nearly three minutes of flushing at approximately 300 scfm were necessary to reduce residual odor from a small explosive sample to a working level.

(f) We also concluded during this phase of our work that humidity level was a factor affecting lingering or residual odor. The higher the humidity, the longer the "flushing period" required. No definitive correlative data were developed however (Figure 3).

In all, this second stage of experimentation was most revealing. As we discovered and corrected (to the extent possible) the problems, we saw the detection level consistently improve to the 90-95% level and false alerts decrease to the 4-7% range.

## Problems

- A. False alerts on food, cosmetics, etc.
- B. Room contamination reduces detection level
- C. Laminar air-flow resulting in "dead spots" at walls
- D. Scent port air velocity—  
low = reduced available vapor - low detection  
high = discomfort to canine - avoidance
- E. Lingering, or residual odor causing false alerts
- F. Humidity necessitates longer "flush" time

Figure 3.

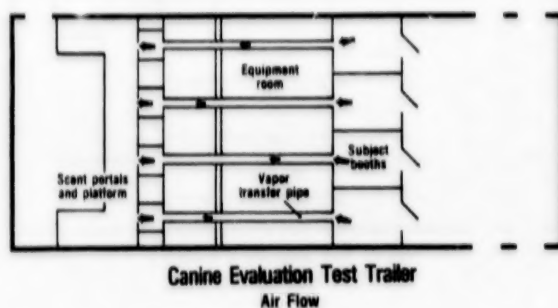


Figure 4.

Again, armed with a plethora of facts, conjectures, and ideas, we entered into the next phase of our experiment. We concluded that the row of four booths had served its purpose and proceeded to refine our design in another area which would provide heavier personnel traffic for full testing of this concept of remote explosive screening. We leased a 12-foot by 40-foot trailer. We placed the personnel search portal in one end and the detection scent ports in the other end of the trailer (Figure 4). On the personnel end of the trailer, we provided doors on both sides of the trailer for two-directional, walk-through traffic. We installed four booths of the same size, construction, and finish as in the earlier phase. We added plexi-glass panels to the doors to accommodate "claustrophobic" complaints that we had received from employees during the earlier test. We also later installed a CCTV monitor in full view of all the booths so personnel could watch the dog work in the other end of the trailer. This kept employee interest up during these sometimes boring and interruptive testing periods (Figure 5).

In the other end of the trailer (the scent port room), we installed four "boxes" along the wall separating the air handling equipment in the middle of the trailer (Figure 6). These boxes were one foot cubes, approximately 55 inches above floor level. Each box had a three-inch inlet hole in the

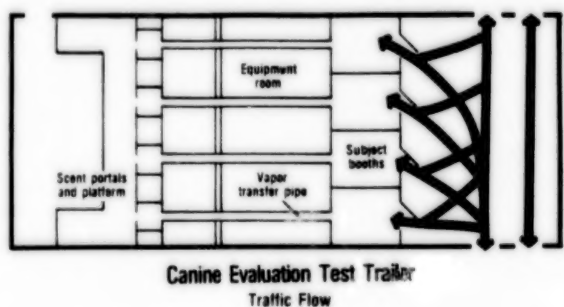
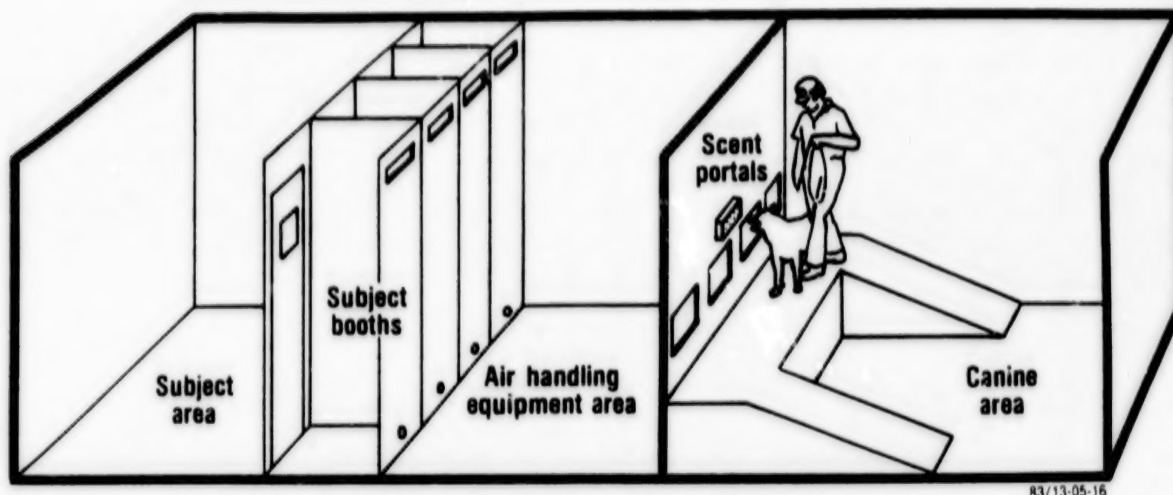


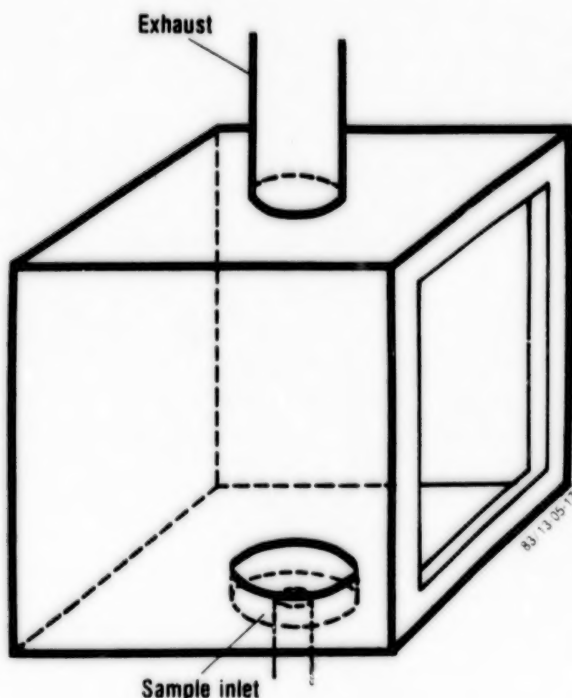
Figure 5.



**Canine Evaluation Test Trailer**  
12-ft. x 40-ft.

Figure 6.

bottom and a four-inch outlet hole in the top. The exposed face of the box was open to the full 12-inch by 12-inch inside dimension (Figure 7). Directly in front of the row of scent ports, we installed a 2½-foot walkway for the canine 30

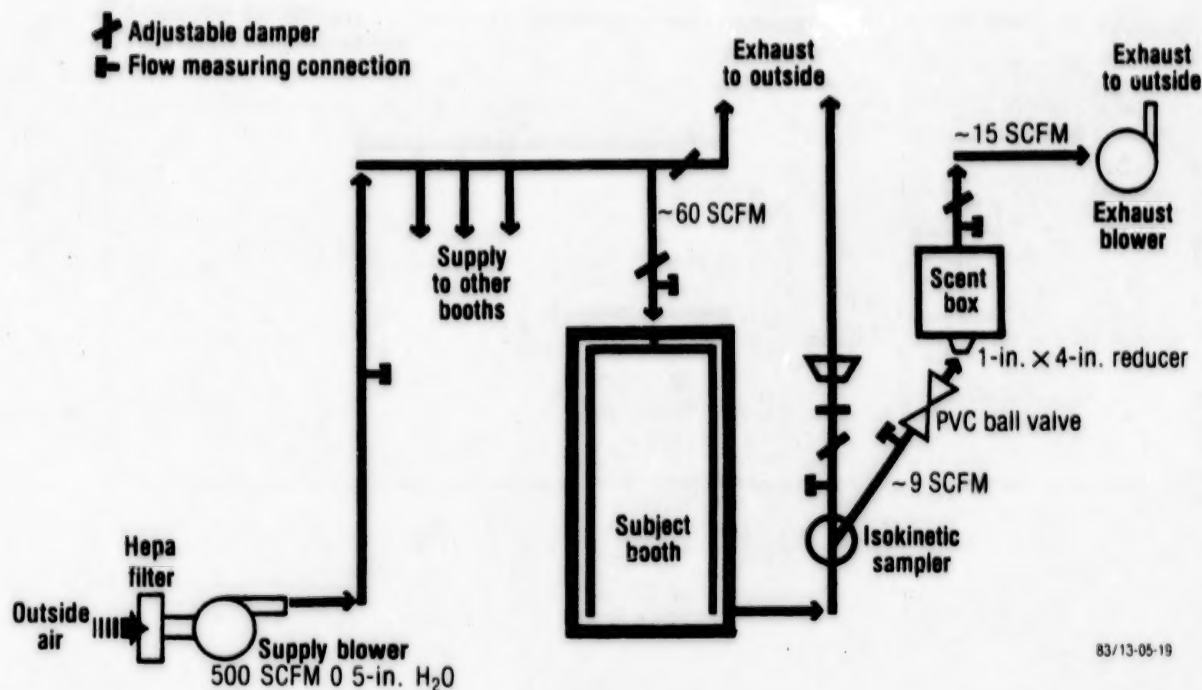


**Scent Port Box**

Figure 7.

inches above the floor level. This enabled the handler to work the canine without stooping over. Ramps at right angle to the walkway were installed at each end to allow the dog easy and safe access to and egress from the walkway. Floor and walkway surfaces were carpeted for noise abatement and safety.

The air movement system was a good deal more complex than in the earlier phases of our work (Figure 8). Fresh air was drawn from the outside and drawn through a HEPA filter by a 500-scfm drum-type blower. The main air supply was manifolded into four 4-inch booth supply pipes. Each pipe was attached to the false top of a booth which served as a booth supply plenum. The booth supply plenum fed four vertical three-inch PVC pipes located in the corners of the booth. The vertical pipes were closed at the booth floor. Holes one inch in diameter were drilled in the vertical pipe pointing toward the middle of the booth where the search subject would stand. A three-inch stainless steel booth exhaust pipe was attached to the back of each booth one inch above the floor level (Figure 9). Exhaust air from the booth traveled approximately twenty feet through the air handling equipment room in the middle of the trailer. Approximately five feet short of the wall separating the equipment room from the scent port room, the booth air exhaust pipe was turned upward in a gentle 48-inch radius, 90° turn. At the point of the turn, a one-inch diameter isokinetic sampler was welded into the three-inch stainless steel pipe with



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## Air Handling System

Figure 8.

an inside protrusion of  $1\frac{1}{2}$  inches. The other end of the isokinetic sampler was attached to a reducer on the bottom of the scent port box. The main four-inch booth exhaust pipe was terminated outside the roof of the trailer and exhaust air released to the environment.

Control dampers were installed at strategic points in the system to:

- (a) Control booth supply air at 100 scfm
- (b) Control main exhaust air at 92 scfm
- (c) Control sample air to scent point at 8 scfm.

We also installed a second exhaust blower to handle the scent port box exhaust air. This was a 100-scfm drum-type blower manifolded on the intake side to the tops of the scent port boxes. Dampers between the scent ports and the manifold controlled air flow to 10-12 scfm. The exhaust side of the blower was directed outside to the environment. What resulted here was the exhausting of the 8-scfm sample tube air along with a small amount of scent port room air thereby precluding vapor contamination of the scent port room itself.

Once we became familiar with the system, we found that we could start up the system, subsequently adjust air flows in approximately 15 minutes, and periodically check them in about five minutes. We recommend communications ability

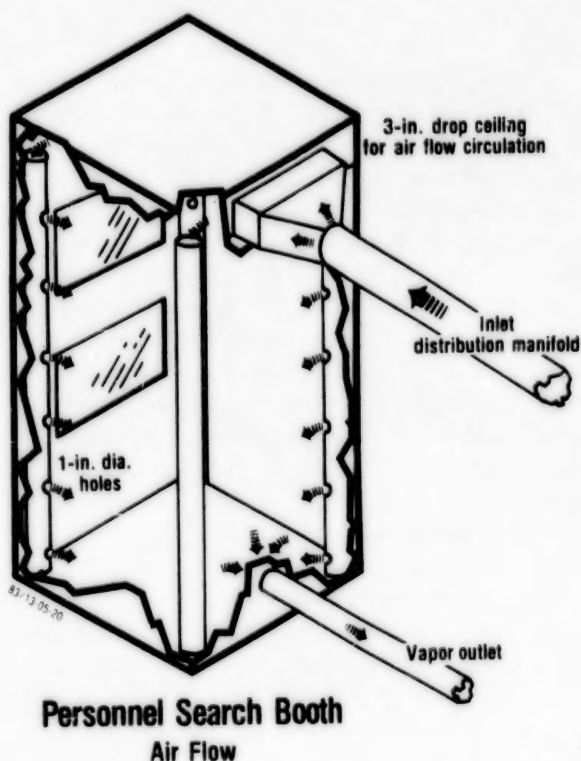


Figure 9.



from the air handling equipment room to both the personnel booth area and the scent port room since in our design some of the control dampers are remote from measuring points. To calibrate the system, we used an anemometer and stop watch.

Before testing this design, we devoted approximately two weeks to acclimating the canine and handler to the scent port room routine, to training the personnel who would conduct the test, and to orienting the employee group to their search-subject role in the test. We chose C-4 (4 ounces) and Commercial Dynamite (20 ounces) as the explosives for the test. All samples were to be hand-carried in waxed paper for this test. Additionally, all search subjects were to carry a piece of waxed paper into the booths. With the help of a statistical consultant, we structured the test and used a random sample schedule prepared by him. The sample schedule provided an overall frequency of approximately one-in-nine plants. Samples and waxed paper were issued to employees some 50 feet away from the trailer and recovered at another point away from the trailer. Search subjects were placed in the booths in groups of four in numerical trial order under the supervision of test personnel. Air was allowed to circulate over the search subjects for 30 seconds prior to the search. After this 30 seconds, the canine sampled the air in each of the scent port boxes in the other end of the trailer. If an alert ensued, the canine handler moved a switch corresponding to the alerted upon booth scent port which illuminated a booth numbered light in the other end of the trailer. The remaining scent port boxes were then investigated by the canine. All positive and negative responses were recorded on data sheets which were given to the statistician for analysis. In addition, the tests were monitored by our Quality Assurance group to ensure strict conformance to the approved Test Plan. The results of this test most encouraging (Figure 10).

*On the Commercial Dynamite:*

Total Number of Trials	720
Number of Explosive Plants	102
Detection Rate	102/102—(100%)
False Alert Rate	18/618—(2.9%)
Total Correct Rate	702/720—(97.5%)

*On the C-4:*

Total Number of Trials	420
Number of Explosive Plants	64
Detection Rate	64/64 —(100%)
False Alert Rate	7/356—(1.9%)
Total Correct Rate	413/420—(98.3%)

These test results reflected a marked improve-

## Phase Two Results

### COMMERCIAL DYNAMITE

Total number of trials	720
Number of explosive plants	102
Detection rate	102 (100%)
False alert rate	18 (2.9%)
Total correct rate	702 (97.5%)

### C-4

Total number of trials	420
Number of explosive plants	64
Detection rate	64 (100%)
False alert rate	7 (1.9%)
Total correct rate	413 (98.3%)

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Figure 10.

ment over the previous phase. We attribute this improvement to the facility design.

We did notice some design deficiencies during the pre-test and test, however.

(a) During rainy or very humid periods, the paper HEPA filter element collected moisture which restricted air flow.

(b) The temperature of the air blowing across the search subjects was at outside ambient temperature which provided discomfort on occasion (*i.e.*, winter mornings and summer afternoons).

Both of the above problems are solvable with the installation of an air conditioning system ahead of the HEPA filter which would assure constant control of humidity and temperature. This air conditioning system must be of the "once-through" design rather than the normal recirculating type with minimal makeup air. This is necessary to preclude the recirculation of explosive-vapor-contaminated air.

(c) While the air in the search booths was mixing well, there were some "dead spots" along the walls of the booth. We were concerned that it might be possible to hold very small amounts of explosives in these areas and avoid detection. This was, in the next phase of the test, easily overcome by drilling 1/2-inch holes in the vertical air supply pipes in the booths. These holes were placed in such a direction as to force air along all four walls inside the booth and in a similar direction (Figure 11).

There was another concern. In addition to the booth air mixing matters that we had been work-

## Problems

- A. Humidity
- B. Temperature
- C. "Dead-spots"

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Figure 11.

ing on, we wondered whether the "once-through" air flow design incorporated in the system was over-diluting explosive vapors in the system when they were present. Based on the results from the previous phase of testing, there was no reason to believe that this was the case. However, because of our concern of very small amounts of explosives carried, we decided to recirculate the booth air in an attempt to minimize dilution and, at the same time, enhance the air-mixing function. To do this, we installed four blowers, one for each booth. The blowers were constant speed and rated at 75 scfm. Air was drawn from two 6-inch ports eight inches above booth floor level, manifolded down into one stream, through the blowers, re-manifolded back into two 6-inch pipes and then back into the booth eight inches below the booth ceiling level.

Unfortunately, the test schedules did not permit the installation of an air conditioning system prior to the third and final testing phase. As a result, we are unable to statistically confirm our conjecture on this point.

During the final testing phase, we held to the same test structure with the physical modifications mentioned earlier and two notable exceptions. This phase of testing was to determine the effects on detection rate and false alert rate when the explosive sample was wrapped and concealed. (You will remember that the samples were "hand-held" in the earlier phase.) In the final phase, four ounces of C-4 were wrapped in heavy gauge, polyethylene bags and concealed in the pockets of clothing. The samples were again randomly placed during the test, and bags were present in all trials. Also, the samples were held in the clothing for randomly selected five-minute time increments ranging from 5 minutes to 20 minutes prior to search. (C-4 was selected because of its low vapor pressure and by request of several federal agencies.) We also reduced the pre-search booth time from 30 seconds to 20 seconds. Budget considerations prevented the testing of more than one explosive type.

The results of this testing phase were as follows:

Total Number of Trials	200	
Number of Explosive Plants	29	
Detection Rate	29/29	—100%
False Alert Rate	1/171	—0.6%
Total Correct Rate	199/200	—99.5%

Likely Bounds (approximately 95% confidence limits)

Total Correct Rate	96.8	—100%
Detection Rate	85.4	—100%
False Alert Rate	0.3	— 4%

Figure 12.

It should be noted that the likely bounds are low because of the small number of samples and trials in the test.

We are therefore assuming that this approach to remote personnel searches for small amounts of explosives provides promising results that meet our criteria of high probability of detection (approximately 100%), low false alert rates (approximately 1%), and expeditious searching of large volumes of people (approximately 20-25 seconds per group of four in the test). [Note: We feel that eight to ten people could be search in eight to ten booths within the 20 to 30 second time frame]. Finally, it appears to be cost effective (one dog and handler during periods of high traffic and one officer and one instrument during low traffic periods).

As a result of some informal testing, and participation in tests conducted by others, we offer some insights to canine-team limitations and program structure.

(1) The same system appears useful for narcotics odors.

(2) For facility operation in all weather conditions, an adequate supply-air conditioning system is essential.

(3) If the canine is to alert on both large and small explosive samples, inside and outside, he must be trained on both large and small samples, inside and outside.

(4) The canine works best "moving" and working continuously. The working environment should be non-confining and active.

(5) Training aids can become cross-contaminated. They should be stored separately and worked separately.

(6) The search team, in an access portal, should be under knowledgeable surveillance. Consistency of speed and commands is important to preclude confusion and boredom in the canine.

(7) The canine-team approach to personnel searches should be used only for high traffic periods. "On-again, off-again" work is difficult for the dog.

(8) On outside or vehicle explosive searching, the experienced handler should plan the search.

Moving any detector dog too quickly into a strong odor is not generally successful.

(9) A quality training, retraining and certification program should be established for canine teams. This will provide documented assurance of initial and continued proficiency.

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## THE SCIENTIFIC DEVELOPMENT OF AN EFFICIENT DETECTOR DOG THROUGH OLFACTION AND BEHAVIORAL MODIFICATION

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and

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**ABSTRACT.** A progressive learning sequence departing from the traditional methods of training dogs results in an olfactory sensitive dog compatible with a learned behavior to communicate recognition of a primary vapor. In essence, the developed dog with a skilled handler becomes a portable, mobile biological vapor detector. The innovative procedure researched and practiced at Southwest Research Institute, San Antonio, Texas, emphasizes timely, positive reinforcement of desired behavior in qualified dogs. Initial methods sensitizes the dogs olfactory system to a practically pure primary odor metered with a nitrogen gas carrier in an olfactometer. The dog then learns an associative behavior which communicates recognition or discrimination of the primary vapor (explosives, narcotics, etc.). A scientifically developed dog, properly managed by an educated handler, can augment any law enforcement team and in a practical sense excel most known mechanical or electronic detection devices. The discussion will feature a research study on the dog's recognition and olfactory sensitiveness to ethylene glycol dinitrate, an insignificant component with respect to quantity in five dynamite samples. Some research studies sponsored by the Department of Defense, Drug Enforcement Agency, Department of the Interior, Department of Agricultural and Industrial Companies will be discussed. Moreover, a casual overview of new work further expanding the usefulness of detector dogs in service to man will be presented.

A dog developed through the steps of olfactory sensitization to a primary odor with concurrent behavioral modification compatible to search and detection procedures is, in due respect, a vapor analyzer. The olfactory dog's speciality is qualitative rather than quantitative analysis with the capability of discrete odor discrimination. The dog learns in sequence, from positive reinforcement, a chain of behavior that eventually directs it to becoming a qualified olfactory detector.

The most difficult and time consuming step in the development of an olfactory dog is in limiting the negative influence of environmental distractions. Distractions disrupt its concentration and may evoke undesired behavior. Distractions are unwanted stimuli. They may be either audio, visual, olfactory, tactual or gustatory. The distractions that are the most disruptive in a practical search and detection exercise, especially in a par-

tially trained dog, are audio, visual, and olfaction. Olfactory distractions are insignificant when the dog becomes accustomed to training. Audio and visual distractions, other than the obvious, may be very subtle signals from the person working the dog. For example, cues from the handler may be intentional or unintentional. They may be obvious or inapparent. Cues from the handler can cause false responses, excitable activity (not to be confused with motivation) or excessive attentiveness to the handler rather than the task at hand. The dog, because of its close relationship to man, is extremely susceptible to any cues that might emanate from the trainer or handler. With respect to olfactory sensitivity, the dog, compared to man, is a privileged animal. In general, a trained dog has a sensitiveness on the order of at least one femtomole ( $10^{-15}$ ) and very probably at a much lesser concentration.



A mistake often made by people is concluding that dogs are unable to detect chemicals that are classed as odorless. This chemical property is in respect to human olfaction and not dogs. A dog's olfactory acuity can be developed to perceive and discriminate sodium chloride, quinine, heroine, some plastic explosives, etc., all of which may be regarded as odorless. Myznikev, Pavlov (1958), Dean (1973, 1975), Phillips and Dean (1973) It has been reported that dogs may detect  $\frac{1}{2}$  million different compounds, while humans may detect only a few thousand; and, yet, it is recognized that the human has a well developed sense of smell. Myznikev, Pavlov (1958)

The dog is classed as a free mouth breather with an extremely well developed olfactory system. Each nostril communicates with four passageways in which air circulates. The nasal septum is on a median plane and laterally separates the nasal passageways. The common nasal passageways lie at right angles to the other three. It is the larger of the nasal passages; but the middle nasal passage, and probably the most significant with respect to olfaction, communicates with the cavities of the ethmotrubinates which contain most of the olfactory receptors and then continues to the nasal pharynx.

The olfactory nerve is not a single nerve but a mass of fiber bundles which arise from the bipolar olfactory cells in the nasal cavities. In a morphological sense, the olfactory nerve is not a nerve as are the other cranial nerves (exclusive of the optic nerve) but, instead, is a modified tract of the brain. Each olfactory receptor is connected to its own nerve fiber which courses uninterrupted without synapsis through the cribriform plate to the olfactory bulb which is the forward extension of the cerebral hemispheres. The receptors do not terminate in a diffuse array but end singly in the glomeruli of the olfactory bulb. Wright (1982)

The ethmotrubinates are bony ridges covered by mucous membranes and occupy the posterior half of the nasal cavities. This is where the bulk of the olfactory cells are located. When the dog sniffs, samples of air are forced over the turbinates, exposing the fine cilia in the moist layer of the mucous membrane. It has been observed that a panting dog with little evidence of sniffing can track a victim at a ground temperature of  $41^{\circ}\text{C}$  and a body temperature of  $41^{\circ}\text{C}$ . This indicates olfactory stimulation via nasal pharynx rather than by the nostrils.

It has been determined that the German Shep-

herd has  $2 \times 10^9$  olfactory receptors and that each cell has 125 cilia. Thus, the total ciliary surface area is on the order of  $7.85 \text{ m}^2$  or several times the area of the dog's body surface area. It has been concluded and recognized by olfactory physiologists that one molecule of a certain vapor is enough to stimulate a single olfactory cell. Moulton (1976)

It appears that each receptor cell functions as an independent unit through which impulses are carried to the brain. There are many theories on olfaction. Of all the expressed theories, there are two which are generally acceptable. They are Amorre's chemical theory and Wright's vibrational theory.

Despite objections in the use of dogs as odor detectors, it is doubtful that while some devices might be more sensitive than the dog, they cannot at this time, in a practical sense, discriminate specific odors as reliably as the dog. A recently developed bioluminescent technique on the West Coast exploiting firefly luciferase as a TNT detector may offer some advantages, providing an air sampling mechanism can be adapted to the luminescent detector for field use. It is claimed that bioluminesces can detect TNT at  $10^{-18} \text{ M}$ .

The primary objective in using dogs as vapor sniffers is to extend man's capabilities beyond the limits of his own. A well trained search and detector team includes a skilled handler and a skilled dog working together. Often the dog is faulted because of irresponsible handling and inept training practices.

Before submitting the dog to a systematic step-by-step learning process, a careful selection procedure is necessary. Only about 33% of the dogs examined become candidates for about 500 hours of training. The length of time may vary depending upon the primary odor to be detected, ultimate task to be performed, and work environment. The hours are not massed together but are spread out over a 12-month period, working from one or more hours per day. The most difficult feature in training a dog is in coupling its natural abilities to a set of predictable behavioral responses acquired through training. It begins with man's ability to shape the dog's behavior through a learning sequence that directs the dog to sniff, search and respond to the primary odor in a working environment.

The objective is to establish a bond between the unconditioned reflexes of the dog to a set of acquired conditioned reflexes. How this is done and



eventually practiced by an animal behaviorist or trainer and handler will influence the reliability and performance of the dog. The canine behaviorist does not adhere strictly to psychology terms but uses terms that, in a practical sense, relate to the learning period, learning exercises, and work environment of the dog—much like the teacher relates to his students.

The characterization that generally makes a dog adaptable to training are mediated through the acquired conditioned reflexes (Pavlov). Conditioned reflexes are either natural or artificial. The natural reflexes are acquired from experiences in association with a viable existence. Artificially acquired reflexes, in this case, are those learned in the process of training. With consistent repetition of training, the learned response reflex becomes almost involuntary (habit). Unconditioned reflexes are native to the animal, for example, locomotor reflexes, alimentary reflexes, respiratory reflexes, pupillary reflexes, etc. Dukes (1977)

When the dog eats, saliva is secreted. This is an unconditioned reflex. Eventually, when the dog sees or smells food, it will secrete saliva. This is a natural conditioned stimulus. At feeding time, the dog learns the noises that are associated with receiving food. For example, opening the feed room door and banging of pans at feeding time will stimulate salivation even though the sight and smell of food are absent. This reflex is an artificial conditioned response. In the development of working olfactory detector dogs, food through the gustatory reflex (the positive behavior reinforcer) is the unconditioned stimulus and the primary odor (dynamite, heroin, oil, etc.) is the artificial, conditioned stimulus. Before the dog can become a working detector, it must learn to search for its odor, overcome strong distracting stimuli because they, themselves, evoke responses, detect the odor stimulus and then signal to the person accompanying it that the target odor has been found.

The principal for development of a detector dog is to shape its behavior to the limit that the learned response becomes nearly habitual. The dog is indoctrinated with small bits of food following the performance of acceptable behavior. The verbal praise, good, is paired with food reinforcement which is similar to the dog's artificially conditioned reflex of salivating when it hears the sounds associated with daily feeding preparations. The verbal praise ultimately has three purposes:

(1) A convenient positive reinforcer in lieu of food (which should not be extensively practiced)

(2) A stop-gap between the time of response and serving of food reward—This is more important in the beginning steps of training. The delay between verbal good and serving of food should be minimal. It is important that the verbal announcement and serving of food be accomplished by the trainer so that this operation is in two distinct steps. If the trainer reaches for the food before announcing "good", the dog will surely cue on the handler's hand. If the handler feeds the dog at the same moment he announces "good", the verbal reinforcement will become meaningless. When the dog becomes familiar with the routine (search, detect, sit, verbal "good", feed), the time between the verbal reinforcement and serving of food can be extended from one or two seconds to five or six seconds. When the delay time of five or six seconds, the dog might verify or re-examine the positive odor. A longer delay time may cause the dog to become impatient.

(3) To facilitate learning when the primary odor is nonvolatile—This is the most difficult form of use of verbal praise. The dog's nose must be positioned over the odor and a "precision guess" that the dog is sniffing at the time the verbal "good" is announced. In a series of trials, the watchful trainer will, on chance alone, announce verbal "good" in a timely manner so that the purpose of the cue will become meaningful to the dog. As with any expedient, the verbal cue should not be overused.

A simplified laboratory behavioral chain is diagrammed to illustrate the alternate management of behaviors during learning exercises.

Figure 2 illustrates a simple 3-choice olfactometer design used in initial olfactory training on a relatively pure primary vapor sample. Three gas sample bottles are prepared. One contains a few ml of the primary odor sample; the remaining two contain negative control samples. Nitrogen gas, at the rate of 10 cc/min. is metered through each one of the three sample bottles and, ultimately, through three separate teflon tubings which are connected to stainless steel or Buchner funnels. The emission of the nitrogen gas odor carrier is then presented in the test odor ports for the dog to sample. When the dog responds to the primary odor at the correct odor port, its behavior is reinforced with food. The odor ports are randomly changed after each trial to confirm that the dog is not position learning and to encourage it to sample all of the test odor ports.

Table 1 is a sample data sheet used to record the

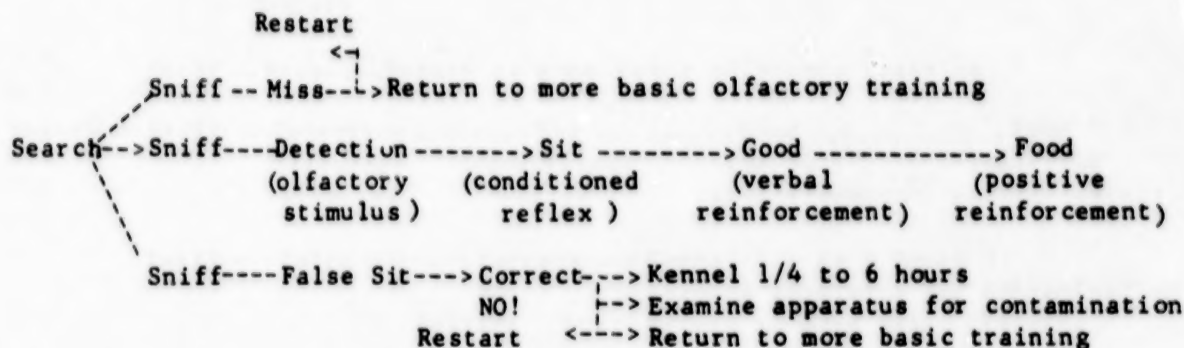


Figure 1. Correction of Alternate Behavior in Beginning Olfactory Training.

dog's progress during olfactory training. The trial number indicates the number of searches for the primary odor. Position number is the location of the primary odor with respect to the two control odors. The need for the position number is to account for the frequent funnel changes in location during the exercise. The designated S +, S -, S - columns maintain a record of the olfactory samplings at each location.

Usually, a learning exercise comprises 25 trials. Ideally the dog should sample the three odor ports or, in a more mechanical sense, take 75 sniffs of which 25 represent the primary odor. Except in a six-choice configuration where two primary odor

samples are placed, the dog starts a new trial after finding the primary odor. A zero is used to record the fact that the dog did not place its nose in the odor port or otherwise did not sample. A negative sign in the score columns indicates that the dog sampled the odor effluent but did not respond which demonstrates odor discrimination. A positive sign indicates the dog's recognition of the odor by sitting at the primary odor port. A positive sign recorded in a S - column is a false sit. An excessive number of false responses (5%) indicates that the apparatus is contaminated, faulty preparation of material, the dog cannot discriminate the primary odor, presences of a behavioral prob-

Table 1. ABRIDGED SAMPLE OF OLFACTORY PROGRESS SHEET

Primary Odor Sample	EGDN Nitrogen Gas	Date _____ Time _____
Control Odor Sample	Distilled Water Nitrogen gas	Dog _____
Concentration	10 <sup>-6</sup>	Handler _____
Gas Flow Rate	N 10cc/min	

Trial No.	Position S+ Primary Odor, e.g., Explosive Heroin, etc.	S+ EGDN + N	Responses	
			S- Distilled H <sub>2</sub> O + N	S- N
1	2	+	-	0
2	1	+	0	0
3	1	+	0	0
4	3	+	-	-
5	2	0	-	+
6	3	+	-	-
7	1	+	0	-
8	3	+	-	-
9	2	+	-	0
10	2	+	0	-
25				
Symbol				
+	Accurate Response	9		
+	False Response			1
0	Did Not Sample	1	4	4
-	Discriminated		6	5
-	Did Not Respond to Primary Odor			

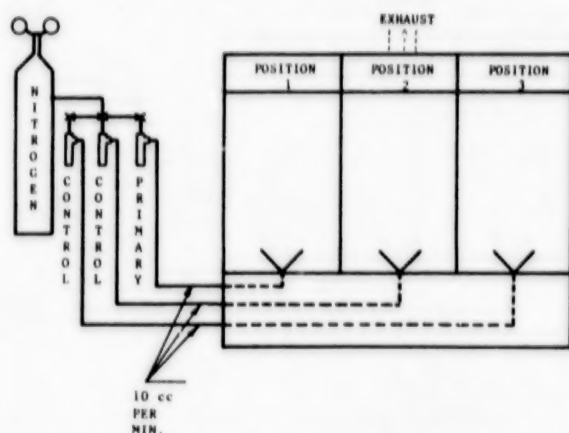


Figure 2. Three-Choice Training Olfactometer.

lem in the dog or poor trainer/handler performance.

During the olfactory sensitivity and discrimination training, approximately 12% of the dogs fail to progress. Failure results mostly from unsatisfactory behavior.

Environmental task training, to some extent, is conducted in parallel with laboratory olfactory training. When the dog is performing near 100% in the laboratory odor detection, field training is emphasized. Field training requires the bulk of the 500 hours; but, once each week, the dog is returned to the laboratory olfactometer for evaluation and reinforcement on the primary odor. Field training requires infinite patience by the trainer, consistent repetition of procedures in different environments (depending on the ultimate task) and application of timeliness.

In our work at SwRI, olfactory sensitivity tests for dynamite were conducted with experienced laboratory dogs. It was of interest to determine the highest dilution of a volatile substance in dynamite that would elicit a trained response in the olfactory dogs. In our early work, an assumption was made that repeated olfactory exposure to dynamite samples eventually would accustom the dogs to respond to an odor profile (a combination of vapors from the ingredients in dynamite) and not to a simple vapor stimulus. For the purpose of the detector dog study, an odor profile considered the following materials: nitrate of soda, ammonium nitrate, wood pulp, sulphur, wood flour, chalk and nitroglycerin (40% extra dynamite). Juhasz *et al.* (1973). However, the results of these experiments showed that a dog can learn to distinguish by olfaction one or two volatiles in a spectrum of volatile components. For example, it was

suspected that nitroglycerine was the principal olfactory stimulant in a dynamite odor profile that caused the dogs to make a positive response upon olfactory sampling. At that time, there was no evidence to indicate that ethylene glycol dinitrate (EGDN) was a major vapor component of dynamite. In a chemical analysis at the U.S. Army Ballistic Laboratory of trapped vapors from five different dynamite samples (100% blasting gelatin, 40% extra dynamite, 60% extra dynamite, ditching dynamite, 60% extra gelatin), ethylene glycol dinitrate was found to be the primary peak in the chromatograms of the volatile components. Chromatographic analysis of the dynamite extract also confirmed the presences of EGDN as well as the nitroglycerine. On a chromatographic scan, at a flow rate of 0.8 ml/min, EGDN emerged in 6 minutes and nitroglycerine at 8.5 min. Juhasz *et al.* (1973)

In a series of olfactory test, the trained dynamite olfactory detector dogs responded to both volatiles, nitroglycerine and EGDN. The difference in the manner of response to the EGDN sample and nitroglycerine sample suggested with a high degree of certainty that the former sample was the primary odor stimulant. Since a pure sample of nitroglycerine was unavailable, fresh medicinal nitroglycerine prells (used in patients with angina pectoris) containing .01 gr. nitroglycerine were used to test the response of the detector dogs upon their sampling of the vapor effluent. Three of the dogs had obvious delayed responses after sampling the prells. The fourth dog did not respond on the first two or three olfactory trials. On the other hand, each of the four dogs immediately responded to the EGDN sample. The results of these tests did not eliminate the probability that nitroglycerine was a part of the dynamite odor profile that stimulated the dogs to respond but, rather, demonstrated that EGDN was the primary olfactory stimulant. If EGDN had been absent in dynamite, then it is reasonable to assume that nitroglycerine would have been the principal odor stimulant.

It was not surprising to learn that EGDN was more volatile than nitroglycerine because of the difference in vapor pressure. Table 2 is reported to show the differences between the two volatiles at scaled temperatures. AMC Pamphlet (1971)

An olfactory experiment was designed to test the dog's olfactory sensitiveness to EGDN by dissolving approximately 7.0 gms. to a one-liter volume of warm distilled water. The molecular



**Table 2. RELATIONSHIP TO VAPOR PRESSURES TO INCREASE IN TEMPERATURE FOR EGDN AND NITROGLYCERINE**

EGDN		Nitroglycerine	
mmHg	°C	mmHg	°C
.038	20	.00025	20
0.26	40	.0024	40
1.3	60	.0188	60
5.9	80	.098	80

weight of EGDN is 152 gms; therefore, 1 ml volume of solution would represent  $4.6 \times 10^{-5}$  M/l. Hence, a 1 ml aliquot of the initial solution delivered to a volume of 1 liter would yield  $4.6 \times 10^{-8}$  M per ml . . .  $4.6 \times 10^{-17}$  M. A 1 ml sample of the represented dilutions was added to a gas diffusion bottle that had a 10 ml/minute nitrogen gas flow. The exhaust flow was delivered through .079 cm Teflon tube to the olfactory sampling funnel for the experienced dogs to sniff. Four trained detector dogs were used in the experiment. The experiment was designed to use a three-choice olfactometer. The two negative control sample bottles were adjusted to an equal nitrogen gas flow rate of 10 ml/min. The negative control bottles contained 1 ml of only distilled water.

Each of the odor sampling ports were at negative pressure so that the sample odor effluent was exhausted to the outside. To prevent room contamination with EGDN, the odor funnels were randomly relocated after one or two trials. The normal or pretest rate of detection efficiency on the dynamite samples was 94% to 99%. Therefore, when the rate of detection efficiency significantly declined during the trials, it was presumed that the dog's olfactory sensitiveness to EGDN at that dilution level had also declined. During the olfactory experiments, each dog, during independent trials, was released to commence its search at the olfactometer. If the animal made the correct response, *i.e.*, sat at the sample odor port, it was positively reinforced. If the dog responded to a negative odor port, it was corrected and scored a false response. If the dog sampled the positive odor port and did not respond at any time during a two-pass search, it was counted as a miss but not as an incorrect response. Each test consisted of 25 trials per dog.

On the average, the results of these laborous tests indicated that the dogs, for the most part, were insensitive to EGDN at dilutions beyond  $10^{-14}$  M. Detection or performance efficiency averaged 85% at dilutions beyond  $10^{-14}$  M. One dog sustained a 98% efficiency rate at  $10^{-17}$  M, but

gave no indication that it could detect EGDN vapors at  $10^{-19}$  M.

An additional experiment with EGDN was conducted at sub-zero temperatures; *i.e.*, the samples and gas and vapor tubing were at  $-30^{\circ}\text{C}$ . These trials were preliminary to transporting dogs from San Antonio to Colorado for the purpose of explosive detection studies in snow and freezing temperatures. Undiluted EGDN samples at sub-zero temperatures in the laboratory presented no difficulty for the EGDN olfactory sensitive dogs.

An epilog to these studies is that the test dog, never having been in snow or sub-zero weather, uneventfully adapted to the environment and, without apparent difficulty, located 96% of the buried surrogate mines containing dynamite and TNT. When a dog was unresponsive at a mine site, it was because the vapors were not available to sample. The mine samples were emplaced six hours before testing.

A translated version of a Russian report further documents the olfactory acuity of dogs in terms of olfactory threshold. Pavlov (1958), Myznikev The literature cites enhanced olfactory sensitivity of service dogs administered either caffeine or amphetamine one hour post-ingestion. Olfactory enhancement persisted for eight hours. Continuous or repeated use of amphetamine markedly reduced the test dog's olfactory capabilities. Bromide used with amphetamine appeared to balance the process of inhibition and excitation in otherwise excitable or apprehensive dogs. Dogs were dosed for 7-10 days. The primary or test odors used in the olfactory threshold tests, as described in the report, were serial dilutions of thymol, acetic acid and ammonia in distilled water.

The results of this experiment showed an increased olfactory threshold value by two to three orders of magnitude over the pre-dose threshold value. For example, in one dog, the pre-dose threshold value for ammonia was  $10^{-10}$  dilution and, after administration of caffeine, the threshold value was  $10^{-13}$ . Doses of amphetamine did not increase the threshold value beyond that which was

achieved by caffeine. In another dog, the caffeine pre-dose threshold of  $10^{-17}$  for ammonia increased to a value of  $10^{-19}$  dilution. The latter test showed that not only did caffeine improve olfactory acuity in the test dog but demonstrated that there are differences in olfactory sensitiveness among dogs of the same breed. Two of the dogs in the experiment demonstrated pre-dose values on the order of  $10^{-24}$ . The pre-dose and post-dose threshold values for each experimental dog were generally consistent with ammonia, acetic acid and thymal dilutions.

The methods used at SwRI for developing olfactory detector dogs have produced dogs of lasting qualities. One dog frequently used in laboratory procedures is 12 years old and, except for slowness, shows only a minor decline in performance. It has been repeatedly demonstrated that dogs can detect a primary odor and individually work, depending on training, in an assortment of task environments. Some of the primary odors we have successfully worked with have been TNT, dynamite, plastic explosives, smokeless gun powder, black gunpowder, Heroin Hcl, and many other narcotics, personnel odor markers, dielectric cable oil, Black Footed Ferret scent and human scent. It might be noteworthy to expand these feasibility studies to include paired odors, for example, guns and emotionally distraught persons or even the odor effluent of radiation sickness. If dogs are to be used in a legal sense, research studies should be conducted to establish evaluation criteria for dog and handler that will eventually lead to bi-annual certification. Through very explicit training and repetition, a good dog can be made a successful and dependable olfactory detector.

The foundation for developing detector dogs is based on positive reinforcement of desired behavior with systematic verbal and food reward. Timeliness, consistency and repetition is of essence. One must remember the basic feature on which sound training can begin—the alimentary reflex is one of the strongest reflexes inborn in the animal. In fact, one of the important criteria for selection of dogs is an overt display of a healthy appetite. The Clever Hans phenomenon (cues)

must be a primary concern during training and during work. Hediger (1981) Although it can never be totally achieved, it is best to develop the detector dog to be as independent as possible of direct handling.

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## INDICATOR TUBES FOR THE DETECTION OF TNT

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and David J. Knight*

**ABSTRACT.** A field detector kit for trinitrotoluene (TNT) in water has been developed at the Naval Weapons Center. In addition, a simple extraction technique has been developed which permits the use of this kit to detect TNT in soil. This kit has been developed in order to assist munitions manufacturers and regulatory organizations in their pollution abatement efforts. Forensic applications are also envisioned when it is necessary to determine if ordnance used to commit a crime contained TNT. The operation of this detector kit involves passing an aqueous solution of TNT through a bisectonal indicator tube. The basic oxide pretreatment section of the tube converts the TNT to its Meisenheimer anion. The indicator section of the tube contains an alkyl quaternary ammonium chloride anion exchange resin which traps the colored anions, forming a stain whose length is proportional to the flow rate, volume, and concentration of the TNT solution. Indicator tubes have been developed for use in two different concentration ranges. The first tube is useful in the 0.1–10.0 ppm range while a low concentration tube is useful in the 10–200 ppb range.

Munitions manufacturers and environmental regulatory agencies need to monitor toxic explosives and their byproducts left in effluent from the manufacturing processes. Also, after an explosive has been used to commit a crime, forensic experts need to identify the explosive from residues in water, soil, or air. A method is needed to provide rapid analysis in the field. This paper describes a method for the analysis of trinitrotoluene (TNT) in water (Heller *et al.* (1982) and Greni and Erickson (1982)). The work described was performed as part of the Pollution Abatement Program at the Naval Weapons Center and was funded under Program Element Number 62765N, NAVSEA Task Area Number SF65572391 under sponsorship of Dr. George Young and under USATHAMA Task Numbers R904.10.0263 and P13 under sponsorship of Captain Peter Rissell.

Before deciding which method could best be adapted to use as a field detector, it was necessary to draft a list of criteria which must be met by any field detector. The detector needs to be portable to permit it to be brought to the sample. The time required to perform the analysis should be of short duration, preferably less than 10 minutes. Many applications have limited quantities of the sample available for analysis, therefore the method should require small sample volumes. Species

which can generally be expected to be present in the sample should not interfere with the analysis. Minimum technical training should be necessary to operate the detector, and the technique should not present a health hazard to the operator.

Currently, a wide variety of analytical techniques are available for the detection of TNT in water. These include oxidation of the solution followed by a colorimetric determination of the nitrate content (Leggett (1977)); extraction of the TNT into an organic phase which is then subjected to a gas chromatographic analysis; reverse-phase high performance liquid chromatographic techniques; electrochemical techniques; and a method in which one monitors the fluorescence quenching of TNT trapped on a fluorescent ion exchange resin (Heller *et al.* (1977)). Few of these techniques can be considered portable as they usually require samples to be collected and sent to a lab for analysis. These methods generally require the operator to have extensive chemical training in order to perform the analysis, and they can all present health hazards to the analyst.

Therefore, we decided to scrap these techniques as possible field methods and look for other possibilities. Health science specialists have used indicator tubes for years to obtain a rapid approximation of the concentration of contaminants in the

air. Such a technique meets our criteria for a field detector.

We have developed an indicator tube for the detection of TNT in water which is based on the formation and subsequent collection of the red Meisenheimer anion. The Meisenheimer anion is formed by treating the TNT with hydroxide ion. The resulting anion is trapped onto a strongly basic anion exchange resin.

The indicator tubes which we have developed are prepared from 4 mm inner diameter (6 mm outer diameter) glass tubing which has a length of 12 cm. These tubes are packed in two sections which are separated and held in place with glass wool plugs. The first or presection consists of glass beads which have been coated with a mixture of calcium, magnesium, and barium oxides. It is in this section that the TNT Meisenheimer is formed. The second or indicator section consists of a quaternary ammonium chloride anion exchange resin. While any strongly basic anion exchange resin will trap the colored TNT anion, many of those available commercially are not adequate for this method since the hydroxide form of these resins is red. We have been using AGMP-1 resin (manufactured by Bio-Rad). This resin is beige in both the chloride and hydroxide forms.

Upon contact with the ion exchange resin, the TNT Meisenheimer anion is trapped forming a red stain (the length is proportional to the solution volume, the flow rate, and the solution concentration). By holding the first two variables constant at 10 ml and 2.7 ml/min, respectively, we are able to use this indicator tube to detect concentrations from 0.1 to 10 ppm TNT in water.

A second indicator tube has been developed to monitor smaller concentrations. This tube uses 1.7 mm inner diameter (7.0 mm outer diameter) capillary glass tubing packed with the same components as the other tube. Using a flow rate of 1.0 ml/min and a 10 ml volume, this tube can be used to detect concentrations between 20 and 200 ppb. Increasing the volume of the sample would enable the analyst to detect even smaller concentrations.

We have designed a kit to enable us to use these indicator tubes in the field. This kit consists of several indicator tubes, a 10 ml syringe, a Swage-lok/Luer-lok coupler, a syringe pump, and a bottle of 1.0 ppm TNT standard. These components are stored in a briefcase for convenience in transporting to the site. For those occasions when electrical power is not available to operate the syringe pump, we also include a power

inverter which can operate from a car battery.

In order to use this kit, the syringe is loaded with the sample and connected to the luer side of the coupler. An indicator tube is connected to the swage side of the connector. This apparatus is then placed on the syringe pump and the proper flow rate is selected. Concentrations are determined by comparison of the stain length with that similarly obtained using TNT standards.

A technique has been developed to use these indicator tubes to determine the TNT content of soil. An aliquot of soil is extracted with an acetone:water mixture. The resulting solution is then filtered and passed through the tube as if it were a water sample.

While we have not attempted the analysis, it is conceivable that these indicator tubes could also be used to monitor TNT vapor in air. An impinger technique could be used to collect an aqueous sample for passing through the indicator tubes. Alternatively, a more direct determination may be possible using tubes containing anion exchange resin which has been wet with a sodium hydroxide solution. This would cause the in situ formation and collection of the TNT Meisenheimer anion. These techniques need to be examined in the future.

Interference studies have been performed using these tubes, stressing the priority pollutants and other explosives. These studies were conducted to determine if the specie of interest stained the resin, reacted with hydroxide to form a compound which would stain the resin, or altered the stain length expected from a TNT standard solution. Several interfering species have been identified. A pH below 6.5 prevents the formation of the TNT Meisenheimer anion. Above a concentration of 2.0 ppm, 2,4-dinitrotoluene produces a green stain on the resin. 2-Amino-4,6-dinitrotoluene also produces a green stain on the resin in concentrations above 10 ppm. These two compounds seem to undergo some sort of chemical reaction with the resin other than an ion exchange reaction. Without the pretreatment section in place, ion exchange reactions occur to form yellow stains from 3,5-dinitro-o-cresol and 4,6-dinitro-o-cresol above concentrations of 100 and 40 ppb, respectively. Red stains are formed in the presence of the presection from 2,4-dinitroaniline and tetraol above concentrations of 0.2 and 0.5 ppm respectively. Except for differing shades of red, these two compounds can not be identified as different from TNT using this method.

Currently, there is no simple mathematical approximation for determining the concentration of a solution directly from its stain length. We believe that this is due to the porosity of the resins which we have been using. With these resins, the TNT Meisenheimer is able to migrate to exchange sites within the resin pores, resulting in a stain that is darker at the front end of the indicator section than further down the tube. This problem could be corrected using a pellicular resin. Advantages of a pellicular resin should be an increase in the stain length, sensitivity, and the linearity of the technique. Disadvantages are that the stain would be lighter due to the decreased number of exchange sites available on the resin, the resin is not commercially available in a useful size range, and these resins are difficult to prepare. Attempts have been made to prepare pellicular resins in the lab by coating inert surfaces with powdered porous resins. Uniform coatings have not yet been achieved, but preliminary data suggest that our assumptions are correct and pellicular resins should solve some of our problems.

The TNT indicator tube kits meet our requirements for a field detector. Future work will be di-

rected towards improving the linearity of the technique. In addition, we plan to develop indicator tubes for the detection of ammonium picrate, tetryl, 2-amino-4,6-dinitrotoluene, nitroglycerine, nitrocellulose, propylene glycol dinitrate, HMX, RDX, and other explosives of military interest found in water.

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# **THE TAGGING OF EXPLOSIVES; THE NEW SWISS LAW ON EXPLOSIVES: DEVELOPMENT, ACHIEVEMENTS AND FIRST EXPERIENCES**

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**ABSTRACT.** In Switzerland the marking of explosives, safety fuses, detonating cords and fusetubes is embodied in law. This act and its administrative rules are herewith presented, completed by the description of the present day situation in Switzerland, the applied investigation procedures for bombings, the efforts taken so far (details on the two systems "MICROTAGGANT" and "EXPLO-TRACER") and future developments.

## **Organization and Function of the Institute of Forensic Science (IFS)**

The Institute of Forensic Science represents a small department consisting of five associates of the Scientific Service, in charge of criminal investigation, of the city police of Zurich. It is directly controlled by the Federal Attorney. Its functions are, among others, to investigate all crimes where explosives are involved all over Switzerland. This includes:

1. The recovery of debris as a result of a bombing on the spot
2. The analysis of all the recovered debris in our laboratories
3. The neutralizing of improvised blasting and incendiary devices (EOD)
4. The instruction and training of all Swiss police corps of the caution to be observed while using explosives in dealing with terrorist bombings

5. The working out of expert's reports for the judicial authorities.

However, it is new for the Institute of Forensic Science to function as the central authority regarding the Swiss Act on explosives.

In this context, we are among other things the authority for—the examination and elaboration of new tagging systems of explosives.

## **The Origin and Implementation of the Act on Explosives**

The Swiss Act on explosives and its administrative rules were put into force on July 1, 1980. The transitional regulations and some prolongations of term led to the fact that the regulations of tagging, in particular, could only have been fully applied since January 1, 1983. This is why we don't have a wide range of experience in the effects of these regulations at this time. The tagging of civilian explosives became a part of the law in

## **THE COMPOSITION OF SEVERAL GELATINE EXPLOSIVES IN % (APPROXIMATELY)**

	Switzerland		Federal Republic of Germany	Italy
	Gamsite A	Telsita	Ammongelit I	Sismic I
Nitroglycol	25	25	38	25
DNT/TNT (Isomers)	6	8	4	9
Nitrocellulose	1	1	2	1
Ammoniumnitrate	61	61	52	60
Wooddust	4	2	4	1
Baricsulphate	3	3	—	4
Ferric oxide	0,5	0,5	0,2	—
Inert (indeterminable)	—	—	—	0.5



Switzerland as a result of the fact that:

- the explosives used for criminal purposes in Switzerland were obtained from more than 90% of civilian sources (refer to Figures 1,2)
- practice has shown that in many cases an analysis of the residual of exploded devices is unsuccessful (*e.g.*, extremely contaminated traces, or traces made useless because of environmental causes, such as water, fire, etc.)
- and, even when the proper testing procedure is employed with such explosive components as PETN, DNT, nitroglycol, ammonia nitrate, etc., the specific origin still cannot be determined. As the following table shows, the chemical composition of various explosives can be similar in one country and likewise, it can be similar in different countries.

### **The Provisions of the Act Concerning the Tagging of Explosives and their Practical Application**

Article 5, Section 3 of the administrative rules on explosives says:

"All explosives must contain a specimen substance by which its origin can be definitely traced, even after the explosive has been detonated. This substance used by the manufacturer for the marking of explosives is subject to a permit, issued by the coordinating office of the Federal Attorney."

Origin is referring to the place of production. In Switzerland, there are four manufacturers and two importers of explosives. According to the legal text, six different marking substances (codes) would be enough.

Even though, in conforming with the legal text, one marking substance or code per manufacturer would be sufficient, we agreed with the manufacturers of tagging substances to automatically send a new code with every new lot. And, in addition to this, we could persuade the manufacturers and importers of explosives to use different codes for some different products.

By the end of 1982, there were 32 different explosives in Switzerland which were tagged with 22 different codes. The total amount of the tagged explosives is between 11 and 50 U.S. tons. As early as the beginning of 1979, we had a meeting with the Swiss manufacturers of explosives. On that occasion we presented the "3M"-MICROTAGGANTS, which was at that time only existing tagging-system for explosives. We informed the manufacturers at that meeting, that we would approve this in the USA developed tagging-system. Exactly two months before the fixed deadline on which the obligation of marking would be put into force, we received from the "Societe Suisse des

Explosifs S.A.," a manufacturer of explosives in the canton of Valais (Switzerland), 50 pounds of the explosive TOVEX A, a water gelatin explosive containing a newly developed tagging substance called EXPLOTRACER.

Even though many of you are familiar with the tagging-substance developed by "3M", I would like for the sake of completeness to briefly present to you the two substances which have been approved so far in Switzerland.

The so-called MICROTAGGANT—the produce of "3M CO.", St. Paul, Minnesota/USA—consists of multilayered melamine resin lamina with a maximum diameter of 800  $\mu\text{m}$  (Figure 3). Nine coloured layers represent the code. These layers are recognizable at a magnification rate of 40 to 100. With these nine layers it is possible to create several hundredthousand combinations or codes. One side of the layer. This enormously facilitates the finding of the particles as well as those in the explosive itself during the recovery. A further lead to recovery and subsequent identification is provided by a magnetic susceptible layer (0 = black). This feature allows for the collection of taggants by use of magnets. Because of the high production costs of the tagging substances (it is being produced exclusively for Switzerland) we obtained approval of an absolute minimal quota of 0,025% within the explosive itself.

The tagging substance EXPLOTRACER from the "Societe Suisse des Explosifs," Gamsen, was developed and produced by the "Plast Laboratories," Bulle/FR, Switzerland (Figure 4). This taggant is based on coloured plastic powder mixed with fluorescent pigments. In order to obtain magnetic susceptible particles, the basic material was mixed with iron powder. Rare-earth elements and other additional substances (inorganic compounds, such as, oxides, etc.), allow for the analytical verification. Thus, it was possible to provide this substance with the same qualities as the "3M" tagging system, especially with respect to recovery and preservation of the particles.

The taggant can be easily detected with the aid of a long-wave ultra-violet light source and can be additionally separated by using magnets to separate from non-magnetic susceptible materials. This EXPLOTRACER is a granulate with grains from 200 to 800  $\mu\text{m}$  which is to be mixed with the explosives at the rate of 0,1%. The various components of this substance: the polymer, the fluorescent pigment and the rare-earth elements and additional substances, provide the code composi-



## THE IFS INVESTIGATION OF BOMBING AND BOMBING ATTEMPTS IN SWITZERLAND DURING 1979 - 1981

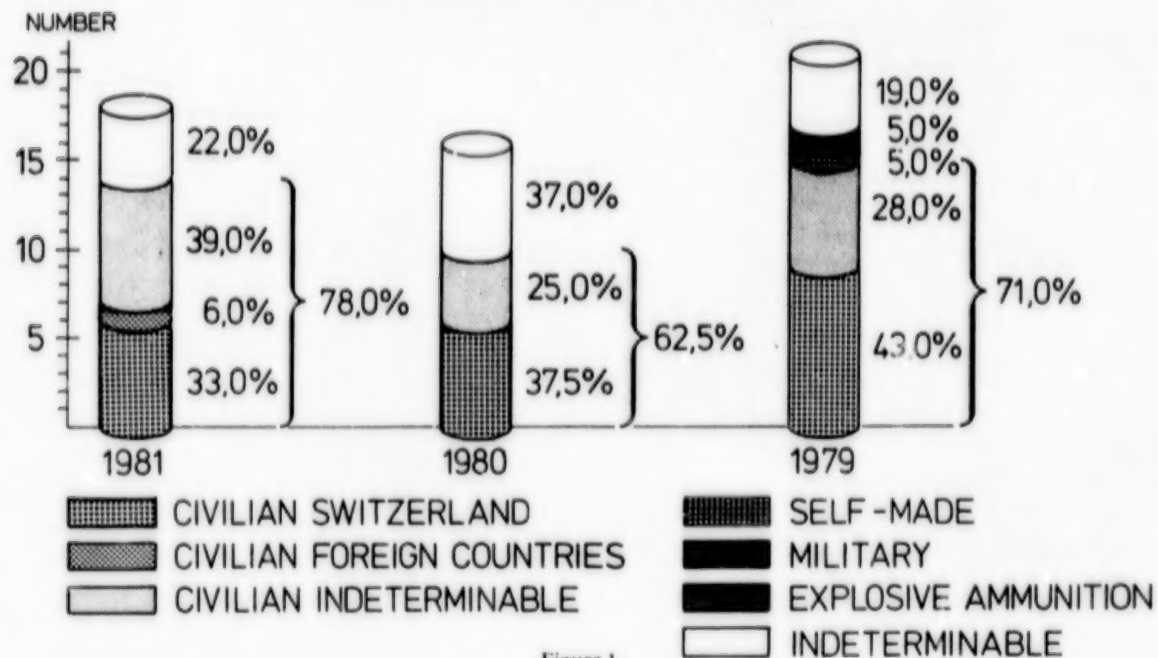


Figure 1.

## SAFE ROBBERIES WITH EXPLOSIVES IN SWITZERLAND DURING 1979 - 1981

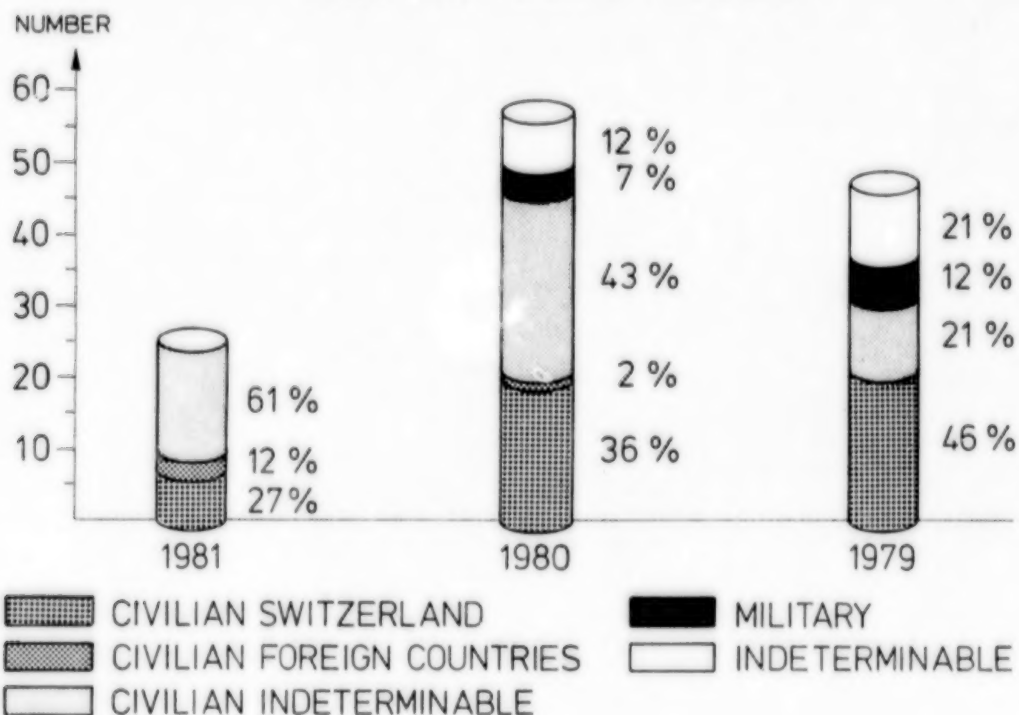
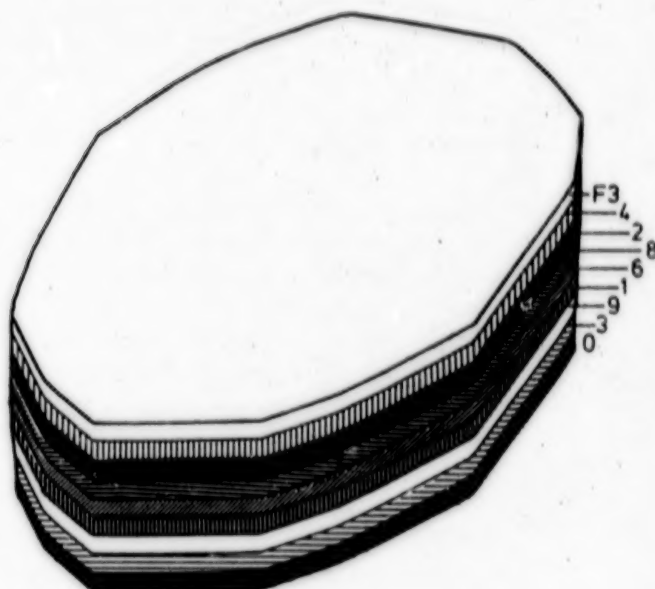


Figure 2.

# MICROTAGGANT

developed by 3M Co., Minnesota / USA



**F 342861930**

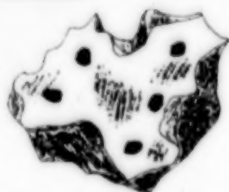
COLOUR - CODE	
0	BLACK
1	BROWN
2	RED
3	ORANGE
4	YELLOW
5	GREEN
6	BLUE
7	VIOLET
8	GREY
9	WHITE

Figure 3.

## EXPLOTRACER

developed by PLAST LABORATORY CO., Bulle / Switzerland

CODE	THOUSAND	HUNDRED	TEN	UNIT
Basic Polymer	1			
Fluorescent Pigment		2		
Rare-Earth Elements			4	
Additional Substances				1



**CODE = 1241**

Figure 4.

tion. If there are ten forms available from every component, there would be a result of almost 10,000 combination possibilities.

The enormous advantage of this system consists of the easy detection of the particles after the explosion. This is due, on one hand, to the relatively large quantity of taggants (0,1%) and on the other hand, to their being completely fluorescent. Their magnetic susceptibility turns out to be less than with the "3M" product because the iron particles mix irregularly with the granulate.

In addition to this, the fact is, that the amount of time necessary to verify and decode these particles is relatively high because they need intensive physical-chemical examination.

The following methods are used to analyze the different components:

- (a) *Plastic powder.* The plastic powders used so far may be differentiated by their melting

points by a thermal analysis or under the polarization microscope.

(b) *Flourescent pigments.* With about five taggants it is possible to produce a thin layer allowing the spectral analyses of the fluorescent pigments within ultra-violet or visual perceptibility of 300 to 600 nm.

(c) *Rare-earth elements and additional substances.* With the aid of an X-ray spectrometer it is possible to analyze rare-earth elements and additional substances (inorganic elements) already with the presence of one single particle.

While this paper was being written, we received a third tagging substance, manufactured by the Haniel Blasting Co., Switzerland. This taggant is not yet fully developed but is similar to the "3M" product which is based on multilayered coloured particles.

Now, let's consider the practical aspect of the preservation of traces. As mentioned above, the so-far admitted taggants are based on fluorescent and magnetic susceptible layers. These two qualities, necessary for the analyses and preservation will be the basic requirements for all further possible taggants. In the meantime, the following methods of preserving traces are useful:

*Procedure A:*

—Collection of single taggants after detecting them with ultra-violet light by means of tweezers, spatula, pointed spoon or magnetic needle.

This method requires almost entire darkness and is very tiring, especially for the eyes. So far, we have been working outside under blankets. Some first trials with boxes equipped with peep-hole and ultra-violet lamps were equally promising.

*Procedure B:*

—Systematic collection by use of magnets.

For this procedure we use magnetic plates, a method already developed by ATF. The use of magnetic plates is an adequate procedure to swab an even surface. To begin, a magnet is placed inside a plastic bag which is used to collect the magnetic particles. To collect the particles, the bag is removed from the magnet by turning it "outside in." In this way, the particles are gathered inside the bag.

*Procedure C:*

—Gathering the particles with the aid of

brooms/brushes of different kinds on dry and even surfaces.

This procedure proves to be inadequate as soon as the surface is damp. A further drawback results in the fact that the brooms are very difficult to clean after use. To prevent any dragging of taggants, it is best to use them only once.

*Procedure D:*

—Wiping the particles off with cotton or cellulose.

This procedure proves adequate for even, as well as damp surfaces. This method is well suited for preserving the explosive residues, as well as the taggants, in one procedure. In the first phase, the surface gets cleaned with cotton and acetone (detachment of the organic components of the explosive) and in a second phase, with cotton and water (detachment of the inorganic components).

*Procedure E:*

—Sucking off with a special vacuum cleaner.

Our vacuum cleaners, developed for the preservations of microtraces, prove to be very useful in the preservation of taggants, too. By the means of a special filter element at the mouth of the vacuum tube or the application of our specially designed broom device, a total success may be guaranteed. The removal of the tiny substances in front of the filter is quite easy and can be controlled.

*Procedure F:*

—Printing off with adhesive tape.

This procedure applied on dry, even surfaces brings excellent results. It is an adequate procedure for small areas in particular. For larger areas, however, this procedure is too complicated. It needs to be taken into consideration that any explosive residues which stick to the tape, may later encounter difficulty, if not an impossibility, to be completely removed from the adhesive of the tape. The debris collected in one or another manner as described, is processed later in the laboratory with customary methods for organic and inorganic explosive substances, such as, the nonexplosives residues.

Depending upon whether microtagging has been found in sufficient number, it is now necessary to proceed with an intensive searching for taggants. For that purpose, the entire collected material and filtrates will be placed by small portions into glass beakers with some water. By means of a magnetic stick, it will be stirred and the magnetic susceptible parts on the stick will be placed into a second glass beaker with water. By removing the magnetic stick

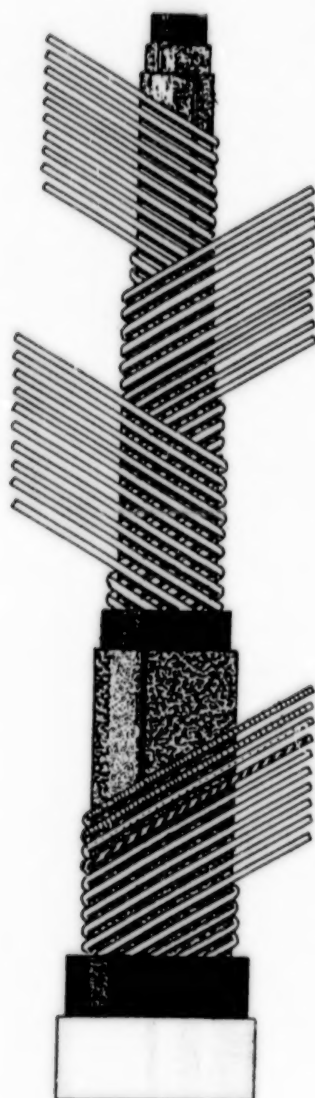
out of its tube, the particles will fall off. This procedure is repeated until all magnetic susceptible particles are transferred. To separate the taggants from the often very numerous extraneous and interfering debris, the materials are transferred into another glass beaker by a further phase. This glass is filled with a solution of sufficient density in accordance with John A. Kearns's method, so that the taggants float. All of the other magnetic susceptible particles do not float; they will sink to the bottom of the glass. With the aid of a long-wave ultra-violet lamp, the fluoreseents will get activated and the taggants can be separated.

In our administrative rules there exist not only rules concerning the tagging of explosives, but also concerning the marking of the most frequent igniters and lighters.

Article 7, Section 1 of the administrative rules on explosives provides the following:

"Safety fuses and detonating cords, as well as fuse tubes, must contain a marker throughout their entire length, which identifies the manufacturer, place, year and month of manufacturer."

Safety fuses have been provided with special marking threads. Figure 5 shows an example of marking colors for the years 1981 to 1982.



COLOUR-CODE			
NUMBER OF THE MARKING THREAD		YEAR (2 THREADS)	MONTH (1 THREAD)
01	BLACK	1981	JANUARY
02	YELLOW	1982	FEBRUARY
03	GREEN	1983	MARCH
04	RED	1984	APRIL
05	LIGHT BLUE	1985	MAY
06	ORANGE	1986	JUNE
07	GREY	1987	JULY
08	PINK	1988	AUGUST
09	BLUE	1989	SEPTEMBER
10	YELLOW-GREEN	1990	OCTOBER
11	BROWN	1991	NOVEMBER
12	VIOLET	1992	DECEMBER

**0204 = 1982 APRIL**

Figure 5.



Twelve marking-thread numbers were combined with 12 well defined colors. By bringing in two threads with the same color, the year is indicated, and with the third colored thread, the month is determined.

The example shows two yellow threads indicating the year of manufacture (1982) and the red thread, the month of manufacture (April).

You may be struck by the fact that the marking threads indicating the date of manufacture are found immediately under the plastic coat. This is according to our requirements because marking threads around the core of the safety fuse cannot be analyzed after it has burned.

The identification of both burned or unburned parts of safety fuses is possible by uncoiling the threads. To decompose the fuse, we put it into xylene.

Explosive cords are partly provided with marking threads, too. As this legal text does not determine the kind of marking, different solutions might be proposed. Figure 6 shows that the markings for the manufacturers have been chosen in

various forms. Thus, for example, two products, such as one explosive cord (Detonex) and the safety fuse (Fritzsche), are marked by additional plastic coats in the cord in place of the colour threads to determine the place of manufacture.

The third article, concerning the marking of explosives, will be found in the administrative rules, Article 9, Section 1:

"On all blasting caps (detonators), electric or non-electric, a marker shall be affixed which identifies the manufacturer, place, year and quarter of manufacture."

This article, the only one of all the rules is not effective up to the present day. The reason is, that in Switzerland there is no manufacturer of blasting caps.

Practice shows, that detonators and blasting electric caps frequently are not totally inserted into the explosive (primarily safe-cracking with the help of explosives) and therefore their rear portion may not be completely destroyed. For this reason, we would like to have the rear portion of detonators provided with specific colours or, in

## MARKING OF DETONATING CORDS AND SAFETY FUSES IN SWITZERLAND

(Situation Oct. 82, Art. 7 Sect.1, Administrative Rules on Explosives)

	MARKING FOR		
	PLACE OF MANUFACTURE	YEAR	MONTH
<b>Detonating Cords</b>			
<b>DETONEX</b> SOCIÉTÉ SUISSE DES EXPLOSIFS, GAMSSEN/CH	PLASTIC WRAP RED-ORANGE	1 COLOURED THREAD IN EXPLOSIVE CORE	1 COLOURED THREAD IN WRAP
<b>DYNACORD</b> DYNAMIT NOBEL AG TROISDORF/FRG	1 MARKING-THREAD RED-VIOLET IN WRAP	2 COLOURED THREADS IN WRAP	1 COLOURED THREAD IN WRAP
<b>TITACORD</b> SOCIÉTÉ DES EXPLOSIFS PONTAILLER S.S./F	1 MARKING THREAD WHITE IN EXPLOSIVE CORE	2 COLOURED THREADS IN EXPLOSIVE CORE	1 COLOURED THREAD IN EXPLOSIVE CORE
<b>DETACORD</b> DYNAMITE S.D.A. UDINE/I	2 MARKING-THREADS RED AND WHITE IN EXPLOSIVE CORE	2 COLOURED THREADS IN WRAP	1 COLOURED THREAD IN WRAP
<b>Safety Fuses</b>			
<b>FRITZSCHE</b> FRITZSCHE, MINUSIO/CH	2 ADDITIONAL PLASTIC COATS IN CORD	2 COLOURED THREADS IN WRAP	1 COLOURED THREAD THREAD IN WRAP

Figure 6.

the case of blasting electric caps, with specifically pigmented stoppers. As I learned at the "3M"-Factory in St. Paul, a spray containing indelible microtaggants is being currently tested. We will examine it further to see whether or not it is suitable for the marking of detonators and blasting electric caps.

### SUMMARY

Finally I'd like to summarize the most important facts in connection with the new provisions:

- The adapted marking provisions in the new act on explosives include all explosives serving civilian purposes, as well as safety fuses and explosive cords and, within a reasonable period of time, detonators and blasting electric caps. We are convinced that this complete tagging and marking system will strengthen and support the evidence.
- The provisions concerning the tagging and marking are based on the fact that in Switzerland, the civilian use of explosives is dominant.
- The tagging and marking provisions required

by the Act are reasonable and economically attainable for the manufacturers and importers of explosives.

—Thanks to our decisions to admit not only one precise marking program, we provoked the development of new systems. And, what's more, we are able to admit, at any time, tagging and marking systems suitable to the specific type of product.

Please, take into account that interested groups could freely purchase unmarked explosives until the end of 1982 (the total of the reported and not yet successfully investigated thefts of civilian explosives amounts to about five U.S. tons, in reality it would be many times that!) We are convinced that these provisions serve the need of our police in order to be more efficient. Though we are aware that now, as before, it is possible to procure or produce unmarked explosives, this should be no reason, however, not to look for new ways to find criminals and terrorists. The real efficiency of our provisions can only be revealed by the future.



**INTERNAL STANDARD CHEMICAL LABELING OF INTACT EXPLOSIVES  
AND THE SUBSEQUENT ONLINE THIN LAYER  
FLAME IONIZATION IDENTIFICATION OF NANOGRAM QUANTITIES  
OF THESE STANDARDS IN SPENT EXPLOSIVE RESIDUES**

*J. Bruce Schlegel, President*

Schlegel Associates, Inc.

in collaboration with

*John M. Newman, Consultant*

Newman-Howells Associates, Ltd.

**ABSTRACT.** It is now possible to analyze quickly and with no laborious sample preparation; non-volatile, high molecular weight complex organic molecules at levels low enough to make chemical labeling of explosives and their subsequent detection feasible to incriminate would be user of explosives in a terroristic manner. First of all, an explosive manufacturer could ID his own product line with a unique, isolated, non-volatile organic chemical of choice to, without doubt, identify his product. Then when utilized for a suspicious purpose, residue samples may be taken on-site and spotted on a Thin Layer Chromatograph with a Flame Ionization Detector. This unit is a turn key automatic system complete with a preprogrammed data system set up for internal standard integrator chromatography analysis showing a CRT and hard copy "hit ratio" percentage of internal standard possibilities in the Basic language software executive. With this technique, the low minimum detectable levels required for a meaningful analysis can be attained. These nanogram or parts per billion levels usually attainable here-to-fore only on volatile compounds that can be gas chromatographed; can now be obtained on non-volatile compounds that will not totally disappear upon explosion. They will be left afterwards to allow tracing of the explosive to the buyer to seller to manufacturer as evidence to prosecute the appropriate guilty party. Preferential Category: 1. Explosive Residue Analysis, 2. Explosive Analysis, 3. Remote Detection of Explosives.

It is now possible to analyze quickly and with no laborious sample preparation; non-volatile, high molecular weight, complex organic molecules at levels low enough to make chemical labeling of explosives and their subsequent detection feasible to incriminate would be users of explosives in a terroristic manner.

First of all, an explosive manufacturer could ID his own product line with a unique, isolated non-volatile organic chemical of choice to, without doubt, identify his product.

Then when utilized for a suspicious purpose, residue samples may be taken on-site and spotted on a Thin Layer Chromatograph with a Flame Ionization Detector. This unit is a turnkey auto-

matic system complete with a preprogrammed data system set up for internal standard integrator chromatography analysis showing a CRT and hard copy "hit ratio" percentage of internal standard possibilities in the Basic Language software executive.

With this technique, the low minimum detectable levels required for a meaningful analysis can be attained. These nanogram or parts per billion levels usually attainable heretofore only on volatile compounds than can be gas chromatographed; can now be obtained on non-volatile compounds that will not totally disappear upon explosion.

These non-volatile compounds will be left afterwards to allow tracing of the explosive to the buy-

er to seller to manufacturer as evidence to prosecute the appropriate guilty party.

The TLC/FID Analyzer offers a unique method to the analyst by combining the universally accepted technique of Thin Layer Chromatography with an automated quantitative detection system based on the classical GC/Flame Ionization principle.

Most separations that are currently performed on conventional TLC plates can be similarly made on the patented TLC rod (Chromarod) with chromatography being effected in the normal manner, by solvent elution. The direct and quantitative detection capability of an FID is applicable to almost all organic substances. It offers an easy, efficient and timesaving method for the laboratory which has requirement to fulfill in this area of operation.

Spot identification transpires without the use of coloring reagents or charring techniques. Peak areas are rapidly integrated and quantitated. Continuous sample throughput permits 10 analyses to be made every 10 minutes. Analysis of organic samples which (a) are not GC volatile, (b) do not absorb UV or Visible Light, (c) do not fluoresce or derivatize easily, can be analyzed.

Screening, OC, fingerprinting, MWD and sample characterization of samples can be performed selectively or as a precursor to further analytical work involving the use of other instrumental techniques for confirmation.

Built-in facilities for direct link to digital/print-out integrator; auto-zero; auxiliary switch for controlling and timing of external triggers are built-in standard to the mainframe of the instrument.

The use of multi-stage solvent development methods offers additional separation flexibility. Also, a programmed pyrolysis device can automatically remove selected sample components from the Chromarod by partial FID scanning prior to allowing subsequent redevelopment of the remaining components contained within a complex mixture.

The Chromarod, 0.9 mm x 152 mm (diameter), has a usable length of 120 mm and is coated with a 75  $\mu$ m layer of specially sintered Silica Gel or Alumina. During the sample scanning process, the rod is automatically re-activated and made ready for repeated use (up to 100 analyses per rod can be made). Since the FID is insensitive to the sintered coating, a firm, straight baseline is achieved with the chromatogram revealing only the quantitative

pattern of the separated components, plus any contaminant present in the sample or solvent system used.

Three types of Chromarods are available; Chromarod-S, S11, and A. Type S and S11 are made from silica gel, the former material having a 85  $\mu$ m particle size with the latter being made from 5  $\mu$ m silica gel particles. Type A is made from alumina, having a 10  $\mu$ m particle size. Material S11 has a greater resolving power for certain classes of chemical substances. The alumina rod is normally used in circumstances where substances are prone to decomposition on silicas. It has also been found that the alumina material is very suitable for samples which fall into the stereoisomer group.

Chromarods can be silver nitrate or boric acid impregnated to enhance certain types of separation.

Sample loading on the Chromarod can range from 2 to 20 micrograms in a spotting solution of 1 to 2 microliters with detection limit in the order of 0.067  $\mu$ g/ $\mu$ l experienced.

Chromarod clean-up and activation is achieved by blank-scanning the rods through the FID and by observing the stability of the meter pointer and/or baseline on a hard copy device. Blank scans may be repeated until meter permanently zeros signifying zero-rod contamination.

After spotting and development, the rods re-activate and self-clean during the sample burn-off (ionization) and are ready for instant repeated use.

Application of the sample requires care. It is recommended that this be undertaken with the aid of a microcapillary tube fitted with an efficient metering device with 1  $\mu$ l being dispensed in five aliquots. Spotting is further aided by the use of the Spotting Guide provided.

Development (15-40 minutes) takes place in a fused plate-glass chamber with the 10 rods (maximum capacity per tray of rods) being retained in the same Rod Holder used for both sample application and scanning procedures.

After development, the mobile phase is removed from the rods by placing the Rod Holder in an air oven for a predetermined period of time, according to the volatility of the solvent used.

The Rod Holder frame is rapidly transferred from the oven to the scanning area of the Chromatograph to avoid atmospheric contamination of the rod coating.

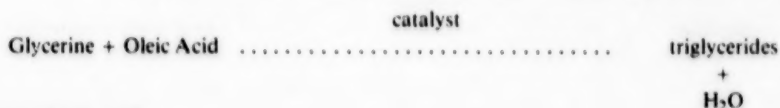
The start button automatically advances the rods in a castellated pattern through to the FID at a constant preselected speed variable by the opera-

tor. The components combust and are ionized to record quantitative individual peak values. Scans can be programmed to combust selected components on a rod, thus leaving those remaining to be further chromatographically developed and scanned.

External electronic integration and print-out systems can be easily connected to the TLC/FID Chromatograph.

Direct quantitation is assisted by adding an internal standard to the sample mixture.

#### EXAMPLE OF ANALYSIS BY TLC/FID CHROMATOGRAPH:



(catalyst is p-toluenesulfonic acid)

A precise volume of the result taken from the above reaction was diluted with chloroform and spotted onto a Chromarod S11 and developed.

Conditions were:

Stationary phase: Chromarod S11  
Mobile phase: Benzene; Chloroform;  
Formic Acid @  
70:30:2 ratio, respectively  
Gas Flow: H<sub>2</sub> @ 160 ml/min.  
Air @ 2.0 l/min.  
Scanning Speed: 30 sec./scan

#### RESULTS: Area%

Rod Number	Tri-Glyceride	Fatty Acid	1, 3 Di-Glyceride	1, 2 Di-Glyceride	Mono-Glyceride
1	11.7	48.9	20.1	7.0	12.3
2	12.2	47.5	22.5	6.9	10.9
3	12.0	49.1	21.7	6.0	11.2
4	11.9	48.9	22.0	6.3	10.9
5	12.5	47.8	21.7	6.7	11.3
6	12.6	48.7	22.0	6.3	10.4
7	11.9	49.0	21.3	6.8	11.0
8	11.6	48.9	21.6	6.4	11.5
9	12.8	48.2	20.8	6.9	11.3
10	12.7	46.7	22.9	6.8	10.8
<hr/>					
$\bar{x}$	12.2	48.4	21.7	6.6	11.2
S.D.	0.43	0.80	0.80	0.33	0.51

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## DETECTION OF GUNSHOT RESIDUES VIA ANALYSIS OF THEIR ORGANIC CONSTITUENTS

I. Jane  
P. G. Brookes  
J. M. F. Douse  
K. A. O'Callaghan

**ABSTRACT.** Procedures for the detection of organic gunshot residues on the hands and clothing of persons suspected of firing a weapon are described. The strongest evidence in this context is produced by using a scanning electron microscope (SEM) to detect metallic primer residues, which have characteristic shape and elemental composition. Unfortunately the SEM procedure is slow and this limits the number of cases that can be examined. Also for some primer compositions the SEM results are not conclusive evidence that the residue arises from a firearm discharge. In an attempt to find an alternative approach that could be used to rapidly screen cases before submission for SEM analysis a study has been made of methods for detecting propellant residues, *e.g.*, nitroglycerine, diphenylamine, nitrocellulose and inorganic nitrite. Capillary GC, TLC and HPLC with electrochemical detection have been used and the conclusions drawn are that nitroglycerine and diphenylamine residues can be determined at low levels which may prove of value, whereas nitrocellulose and nitrite are less promising. The initial levels of residue deposited vary considerably with the types of weapon and ammunition used. Some combinations produced so little contamination that residues could only be detected, using current methods, if the firer was sampled immediately, whereas others produced a high discharge and nitroglycerine, on hands and clothes, and diphenylamine, on clothes, could be detected up to 4 hours after firing. Organic gunshot residue analysis has a future in forensic science but we must improve the sensitivity and selectivity of our techniques before it is routinely applicable.

### INTRODUCTION

During the discharge of a weapon, residues originating from the primer, propellants, lubricants and bullet are deposited on the hands and clothes of the firer. If these gunshot residues (GSR) can be detected on the hands or clothes of a suspect then this will provide significant evidence. Early tests for residues relied on the detection of nitrite ions (Sinha and Misra 1971) but recent and more reliable methods are based on the detection of inorganic residue containing antimony, barium, lead and copper originating from the primer or the bullet. Neutron activation analysis (NAA), atomic absorption spectroscopy (AAS) (Kinard and Lundy 1975) and scanning electron microscopy (SEM) (Wolten *et al.* 1979a) are the most commonly used methods of inorganic residue detection. Of these SEM provides the most signifi-

cant evidence and is the technique routinely used at the Metropolitan Police Forensic Science Laboratory. The particles detected from the primer residue are usually spherical and contain lead, antimony and barium; Wolten *et al.* (1979b) have shown that these particles arise solely from the discharge of a firearm. However the SEM technique is very time consuming and is only applicable if a limited number of samples are routinely received. In addition some priming compositions, particularly those in .22 rimfire cartridges, contain no antimony and the residue from these has a much lower evidential value. To date no one has reported the routine detection of organic propellant residues on the hands and clothes of the firer although detection of these would provide significant evidence of association with the discharge of a firearm. Additionally, since organic residue de-



tection of the primer residue would be non-destructive, it could possibly be used as a screen, prior to SEM analysis to eliminate any totally negative samples.

Modern smokeless powder propellants are based on nitrocellulose (NC), usually in a granular form, with additions of other organic compounds to improve the physical, chemical or mechanical properties of the powder (Mach *et al.* (1978a). The majority of powders in common use are double-based, that is they contain nitroglycerine (NG) as a second major constituent, but single base (NC as the only major constituent) powders are also used. Mach *et al.* (1978a, b) used gas chromatograph/mass spectrometry to study the feasibility of detecting GSR by analysis of the organic constituents of the residue; they were unable to detect any residues using their technique. More recently, various workers have shown that significant quantities of propellant residues can be detected on the firer's hand. Douse (1982) used capillary gas chromatography with electron capture detection (GC/ECD) and thin layer chromatograph (TLC) to detect NG and NC respectively; Bratin *et al.* (1981) used high performance liquid chromatography (HPLC) with reductive mode electrochemical detection, to detect NG and 2,4-dinitrotoluene and oxidative mode to detect diphenylamine (DPA); and Lloyd (1983) used HPLC with polarographic detection to measure NG.

We decided, therefore, to investigate the possibility of using propellant residues to characterise GSR. Rather than attempt to measure all the components present in propellants, we concentrated on NC, present in every smokeless powder, and on NG and DPA which occur in the majority of powders and for which we had sensitive analytical techniques. In addition we measured nitrite since its detection was the basis of many of the earlier methods of GSR analysis and we were able to characterise it using the same HPLC system as we used for DPA.

Although the most significant evidence for having fired a weapon must come from GSR on the suspect's hands, persistence of the residue is much greater on clothes. In the majority of cases at our Laboratory where GSR have been detected it has been on the suspects' clothing rather than their hands. We therefore investigated GSR levels on both the hands and clothes and also in the firer's hair, a further area indicated by SEM results to be a useful reservoir of particulate residue.

## EXPERIMENTAL

### Reagents

NG and NC samples were pure explosives standards (Propellants, Explosives and Rocket Motor Establishment, Waltham Abbey, Great Britain).

DPA was a reagent grade chemical (Harrington Brothers Ltd., London, Great Britain). Other chemicals were reagent grade (May and Baker Ltd., Dagenham, Great Britain).

Diethyl ether, Analar grade (BDH, Poole, Great Britain), was glass distilled prior to use. Methanol was HPLC grade (Fisons, Loughborough, Great Britain). All other solvents were pesticide grade (Fisons). Amberlite XAD-7 (20-50 mesh) (BDH, Dorset, Great Britain) was washed with distilled water, methanol, ethyl acetate, ether and pentane prior to use. Cotton wool (Vestric, London, Great Britain) was soxhlet extracted with ether for four hours.

### WEAPONS AND AMMUNITION

Weapons used in our investigation were:

Smith and Wesson Model 19-3 .357 Magnum revolver with 2½-inch barrel.

Smith and Wesson Model 27-2 .357 Magnum revolver with 6-inch barrel.

Beretta Model 71 .22LR self loading pistol.

Sawn-off Fabrique Nabinale-Browning 12-bore double barrelled over and under shotgun, barrel length 15 inches.

Ammunition fired in these guns was:

Winchester-Western .38 Special, 158 grain round nose lead.

Smith and Wesson .357 Magnum, 158 grain jacketed soft point.

Western 'Super-X' .357 Magnum, 158 grain 'Lubaby' semiwadcutter.

Eley 'Club' .22LR

Winchester 'Super-X' .22LR

Lapua .22LR

Eley 'Grand Prix' 12-bore

Laboratory loaded .38 Special containing:

20 mg Rhodamine B (BDH)

8.5 grains Blue Dot (Hercules, Wilmington, Delaware, USA)

158 grain jacketed soft point bullet

Laboratory loaded 12-bore cartridges containing:

60 mg Rhodamine B (BDH)

20 grains Red Dot (Hercules)

Mark III Plaswad (Plaswad, Beeston, Great Britain)

1½ ounces lead shot.



### Firing Conditions

The firings were conducted in a 25-meter indoor range. Air extractor fans were used to clear the air before each test but were turned off during firing. Weapons were fired from the instructive position, that is with the gun held at waist height.

Sampling for GSR was carried out in a section of the laboratory remote from the range in order to avoid contamination, and this necessitated a minimum delay of five minutes between firing and sampling.

During the experiments with dye loaded cartridges the firer wore a disposable 'waxed' paper overall and paper toweling around the head. After firing, the dye was visualised by spraying the areas of interest with deionised water and viewing them under a long wave ultra-violet lamp.

*N.B.* During a number of these tests using the dye loaded cartridges, bullets were retained in the barrel. This is a hazardous phenomenon and was almost certainly the result of using a reduced propellant charge in these cartridges.

### Analysis of NG and NC

The analysis of NG by GC/ECD and TLC, and of NC by TLC, was performed using the method described by Douse (1982).

#### GC/ECD:

The gas chromatograph (Varian Model 1800) was used with a home-made glass lined injection port and a Carlo Erba Model HT-25 Electron Capture Detector operated in the constant current mode at a potential of 50V and a pulse width of 1  $\mu$  sec. Conditions: column 21 m x 0.25 mm (i.d.) flexible-fused silica capillary externally coated with polyimide (Phase Separations Ltd., Queensferry, Great Britain); stationary phase, OV 101; injection port temperature, 165°C; detector temperature 250°C; temperature program, 25°C held for 30 sec then programmed at 40°C/min to 200°C, cool down time 4 min; carrier gas, helium at 30 ml/min (25°C); make-up gas 5% methane-argon at 13 ml/min; injection solvent, ether or ethyl acetate, usually 0.5  $\mu$ l.

#### TLC:

TLC plates were DC-Alufolien Kieselgel 60F 254 (5 cm x 7.5 cm x 0.2 mm) (Merck, Darmstadt, G.F.R.). The eluting solvent for NG was toluene/cyclohexane (7/3 by volume) and for NC acetone/methanol (3/2 by volume).

Location was by Griess reagent spray. The plates were eluted and the solvent evaporated using a stream of warm air. They were then sprayed

with 1N sodium hydroxide solution and heated to 150°C for 5 min. The plates were then sprayed with a solution of sulphanilamide (8 g) and N-1-naphthylethylenediamine dihydrochloride (0.4 g) (Sigma, Poole, Great Britain) in 8% orthophosphoric acid (100 ml). NC and NG both developed a red colouration.

### ANALYSIS OF DPA AND NITRITE

DPA and nitrite were analysed by HPLC with oxidative mode electrochemical detection, using a strong anion-exchange column where both were to be detected and reverse phase column for DPA alone.

The conditions for DPA and nitrite analysis were:

Pump, single piston reciprocating pump (Model 400, Applied Chromatography Systems Ltd., Luton, Great Britain); column, 12.5 cm x 4.9 mm (i.d.) stainless steel tube slurry packed with a silica-based strong anion exchanger prepared by the method of Wheals (1983); injector, valve injector fitted with a 20  $\mu$ l loop (Negretti and Zambra, Southampton, Great Britain); eluent, 1.75 g of citric acid dissolved in 2.5 l of methanol/water (55/45 by volume), the solution being adjusted to pH 5.5 with ammonium hydroxide solution; flow, 1 ml/min; injection, samples dissolved in eluent.

The eluent was monitored with an oxidative mode electrochemical detector at 0.8 V applied potential versus a silver/silver chloride reference electrode. The detector cell was laboratory constructed (White 1979) with a glassy carbon working electrode; the electronics unit was a commercial potentiostat (Model 174A, EG & G Princeton Applied Research Ltd., Bracknell, Berks., Great Britain).

For DPA alone the conditions were identical except that the column packing was Spherisorb (Phase Separations Ltd.) and the eluent methanol/H<sub>2</sub>O ratio was 65/35.

### Sampling from Hands

Hand swabs were obtained by repeatedly scrubbing the back of the firing hand using a cotton wool swab (approx. 40 mg) moistened with ether. The swab was extracted by successive washing with small portions of ether (total volume 12 ml) in a beaker using a glass rod. The combined extracts were centrifuged to remove traces of skin debris, and the clear supernatant decanted into a silanized conical tube. The ether was evaporated down to near dryness using a stream of nitrogen and the last traces allowed to evaporate at room

temperature. Pentane (3 ml) was added to the residue and the resulting solution transferred to a screw capped vial containing Amberlite XAD-7 beads (10 mg dry weight). The resulting mixture was shaken for 15 minutes so that the beads circulated throughout the solution. The pentane was then decanted using a pasteur pipette and the beads thoroughly rinsed using clean pentane.

The residual traces of pentane were removed with a stream of nitrogen and the dry beads transferred to a clean vial. The beads were then extracted with 50  $\mu$ l of ethyl acetate and 1  $\mu$ l of this extract was analysed for NG by GC/ECD.

For the detection of NC, the insoluble residue from the swab was extracted with acetone. The acetone was then concentrated to low volume and analysed by TLC.

#### Sampling from Clothes

Residues from clothes were collected by vacuuming using the barrel of a 2 ml glass Luer-Lock syringe. (Chance Brothers, Malvern Link, Worcestershire, Great Britain) which was attached to the laboratory vacuum line by the syringe Luer-fitting. A glass-fibre disc (Type AP-Prefilter, Millipore Corporation, Bedford, Massachusetts, USA), cut to slightly greater size than the syringe barrel and pushed firmly on to the base of the syringe, served to retain the particulate matter.

When each sampling was finished the syringe was detached from the vacuum line and the Luer end was sealed with a PTFE plug. Redistilled ether (2 ml) was added and the syringe allowed to stand for 10 minutes to extract the residue. The PTFE plug was removed, the ether was drained into a 10 ml glass evaporation tube and concentrated to approximately 100  $\mu$ l under a stream of nitrogen.

An aliquot of this concentrate was then injected into the GC/ECD for analysis of NG. The remainder was allowed to evaporate to dryness and the resulting residue taken up in 100  $\mu$ l of HPLC eluent for the analysis of DPA.

If an analysis for NC was to be carried out, the glass fibre filter paper was removed and extracted in an ultrasonic bath for 10 minutes in acetone. The acetone was then removed, evaporated to virtual dryness and applied to the TLC plate.

#### Results and Discussion

Preliminary trials with both revolvers and shotguns using cartridges loaded with a mixture of propellant and dye indicated that the main areas where the propellant residues were deposited were

the firing hand, the arms and the front of the chest.

The quantity and position of the dye deposited varied with weapons used. For instance the quantity deposited on the firer by single- and double-barreled shotguns was less than with revolvers, unless the shotguns were opened directly after firing allowing residues to escape from the otherwise sealed breech.

Dye was found on the head of the firer but in smaller quantities than in other areas. Indeed, in later trials with normal ammunition, we were unable to detect any propellant residue on the firer's hair even though this is a site where inorganic residues have regularly been detected in routine casework using the SEM/EDX technique.

As a result of these initial trials two main areas were chosen for examination, the back of the firing hand and the clothing on the arms and the front of the chest.

#### Nitrite Analysis

The use of a strong anion exchange column packing which additionally exhibited a degree of reverse phase retention (Wheals 1983) permitted

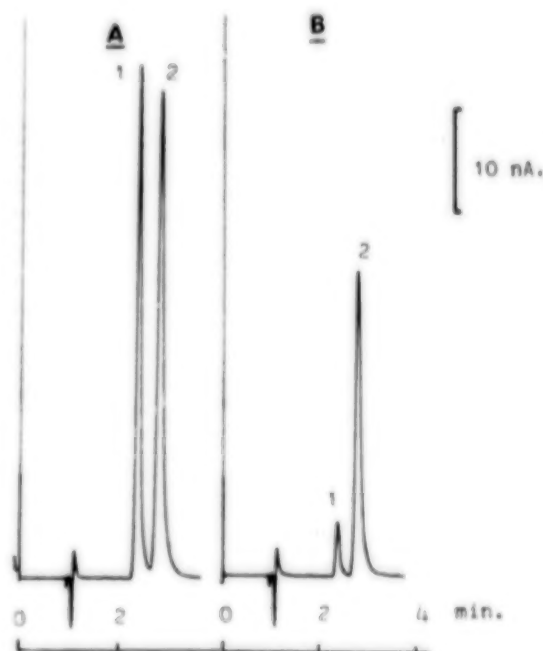


Figure 1. Analysis of DPA and nitrite by HPLC on a strong anion exchange column with oxidative mode electrochemical detection at +0.8 V applied potential. A-20  $\mu$ l of a solution of nitrite (1) and DPA (2) each at 0.5  $\mu$ g/ml in eluent. B-20  $\mu$ l of a 100  $\mu$ g/ml solution of Winchester and Western .357 magnum propellant, sample originally dissolved at 1 mg/ml in ethyl acetate and diluted to 100  $\mu$ g/ml with eluent. Experimental conditions as described in text.

the characterisation of both nitrite and DPA in a single chromatographic analysis. Both compounds are readily oxidized and can be detected with excellent sensitivity by an oxidative mode electrochemical detector (Figure 1).

Nitrite is however an environmental contaminant and initial tests showed that levels of nitrite found on either the hands or clothes of subjects who had fired a gun were *not* significantly higher than those found before firing. This confirms previous experiences where attempts had been made to use the presence of nitrite on the hand of a suspect as evidence of use of a firearm (Sinha and Misra 1971). The work on the analysis of nitrite was not pursued in the context of such evidence, but the method could still be potentially useful in monitoring the stability of NC in propellants by virtue of the nitrite produced by its decomposition.

To eliminate interference from nitrite, the system which was subsequently used for the analysis of DPA was a conventional reverse phase column on which the nitrite was not retained.

#### **Hand Samples**

Unless a high level of GSR was present on the subject's hands (levels corresponding to those on samples taken immediately after firing) NC and DPA were not detectable using present methods; NC because of the relative insensitivity of the TLC technique and DPA because of interference from contaminants in the hand swab extracts. Hand swab samples were, therefore, normally only analysed for NG. The levels of NG found on the back of the firing hand, sampled almost immediately after firing, varied from 2  $\mu\text{g}$  to below the detection limit of the method depending on the weapon and ammunition used.

In an attempt to determine the nature of the residue deposited on the hand, some experiments were carried out in which samples were taken by vacuuming the back of the firing hand prior to the normal swabbing procedure. Similar amounts of NG were found in the hand swab and in vacuum samples from hands immediately after firing. NG was not detected in the vacuum samples from hands taken  $\frac{1}{2}$  hour or longer after firing, despite considerable quantities still being detected on hand swabs. These results indicate that NG is deposited on the hand as both fume and particulate matter, the latter falling rapidly from the hand with normal activity. Figure 2 shows chromatograms of NG recovered from the hands of subjects up to two hours after they had fired a revolver.

#### **Clothes Samples**

The vacuum sampling technique is simple and rapid and provides relatively uncontaminated samples of GSR for analysis. NG, DPA and NC can all be detected at low levels without a sample clean-up. The sampling certainly appears to be efficient since no further residue has been detected on a second sampling. However, the nature of the technique is such that only particulate GSR or particulate matter coated with NG can be detected.

The initial levels of NG found on clothes samples varied from 11  $\mu\text{g}$  to a level below the detection limit of the method, depending on the weapon and ammunition used. Almost invariably higher quantities of GSR were detected on clothes than on hands and the persistence was much greater.

Figures 3 and 4 show NG and DPA levels found on clothes samples six hours after a weapon had been fired. NC on clothes was also detectable by TLC for several hours after the firing had taken place.

The ratio of NG to DPA in samples taken from clothing after 20 firing experiments using the Smith and Wesson model 19 revolver ranged from 10 to 65 with an average value of 27. The average NG/DPA ratio in the original propellant extracted from three unfired cartridges was 49 (44–55).

It is not apparent from the results so far whether the variation in the ratio is due to processes at work during firing or some feature of the sampling technique.

#### **Factors Affecting the Level of GSR Found**

The factors which affect the level of organic GSR found on a firer are numerous and would seem to be similar to those reported for primer residues (Cornelis and Timperman 1974). In experiments to show the effect of one particular factor it is necessary to perform many replicate firings while rigorously controlling all the other variables.

In this initial investigation it has not been possible to do more than verify that the most important factors have the effects that both logic and the results of previous trials would suggest. The factors which, from our experiments, had a considerable effect on GSR levels were: the type of weapon; ammunition; nature of the skin and clothes, and the time and activity since firing.

#### **Type of Weapon**

Weapons which produce discharge from the breech would be expected to give rise to higher levels of detectable GSR on the firer than those in

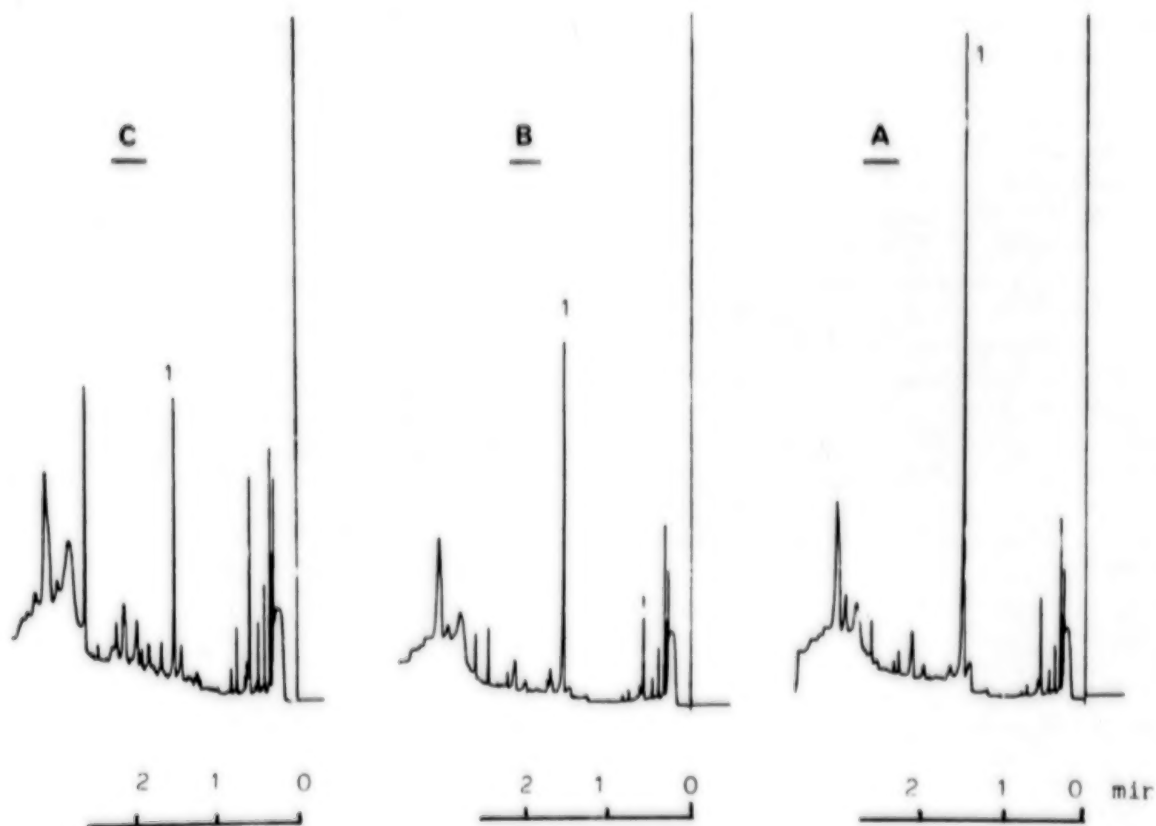


Figure 2. Nitroglycerine from hands using GC/ECD. Three subjects each fired three rounds of Winchester .38 Special ammunition from a Smith and Wesson Model 19 revolver. A-sampled after  $\frac{1}{2}$  hour (corresponds to 140 ng of NG (1) on the hand), B-sampled after 1 hour (78 ng NG), C-samples after 2 hours (10 ng NG). Conditions as in text.

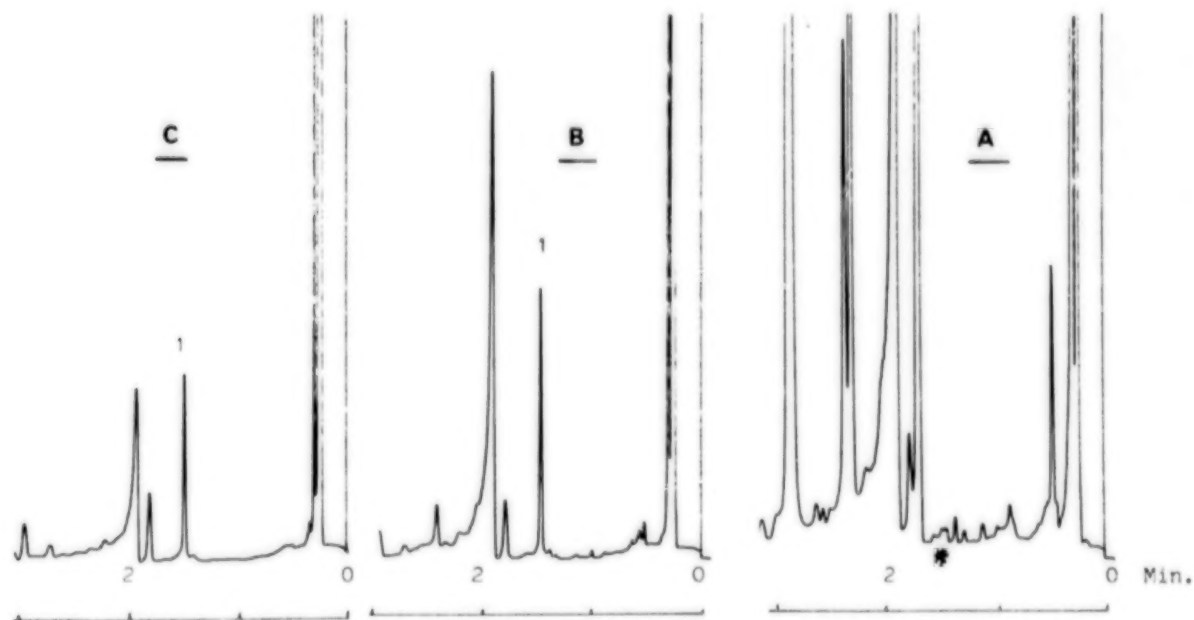


Figure 3. Nitroglycerine (1) from clothes using GC/ECD. A-Blank wool sweater extract,  $\frac{1}{100}$  of sample injected (\* NG retention distance). B-Wool sweater extract 6 hours after firing 5 rounds of Winchester and Western Magnum .357 ammunition from a Model 19 revolver,  $\frac{1}{1000}$  of sample injected. C-100 pg of NG injected. Peaks other than NG in B & C arise from a dirty injection port.

which all the residue is discharged from the muzzle, and this was indeed found to be the case. Revolvers produced high initial levels of GSR, up to 11  $\mu\text{g}$  NG on clothes and 2  $\mu\text{g}$  on hands, whereas sealed breech shotguns and rifles gave very low or even undetectable amounts unless the breech was opened soon after firing the weapon. The cleanliness of the weapon prior to firing will almost certainly affect the nature and amount of residue deposited on the firer; however, we have not as yet investigated this area. The correlation between the composition of the propellant and the composition of the resulting organic residue is another area which remains to be investigated.

The number of rounds fired did not seem to have a marked effect on the quantity of residues detected; this result agrees with that reported for primer residues by Cornelis and Timperman (1974) but it is perhaps an unexpected one and merits a more rigorous investigation.

#### Nature of Skin or Clothes

Samples taken from clothes made of materials which trap particulate matter show higher initial

levels and greater persistence of organic GSR than clothes made from 'smooth' materials. The initial levels of GSR detected on hands varied considerably both between subjects and on the same subject on different days. This was true even when all other controllable variables were kept constant. This variation would seem to be due to variation in the skin condition and other related factors.

#### Time and Activity Between Firing and Sampling

In the experiments to determine the persistence of organic GSR the firers were asked to behave normally between firing and sampling but *not* to wash their hands. With hand samples, a rapid initial loss of GSR was observed followed by a slightly less rapid loss of the remaining residue. From our results we would expect to be able to detect NG on the hand of a firer some two hours after firing a revolver.

The persistence of GSR on clothes is much greater. In tests where firings were carried out with a revolver, we were able to detect NG, DPA and NC six hours after the firings had taken place with the subjects wearing a variety of clothes.

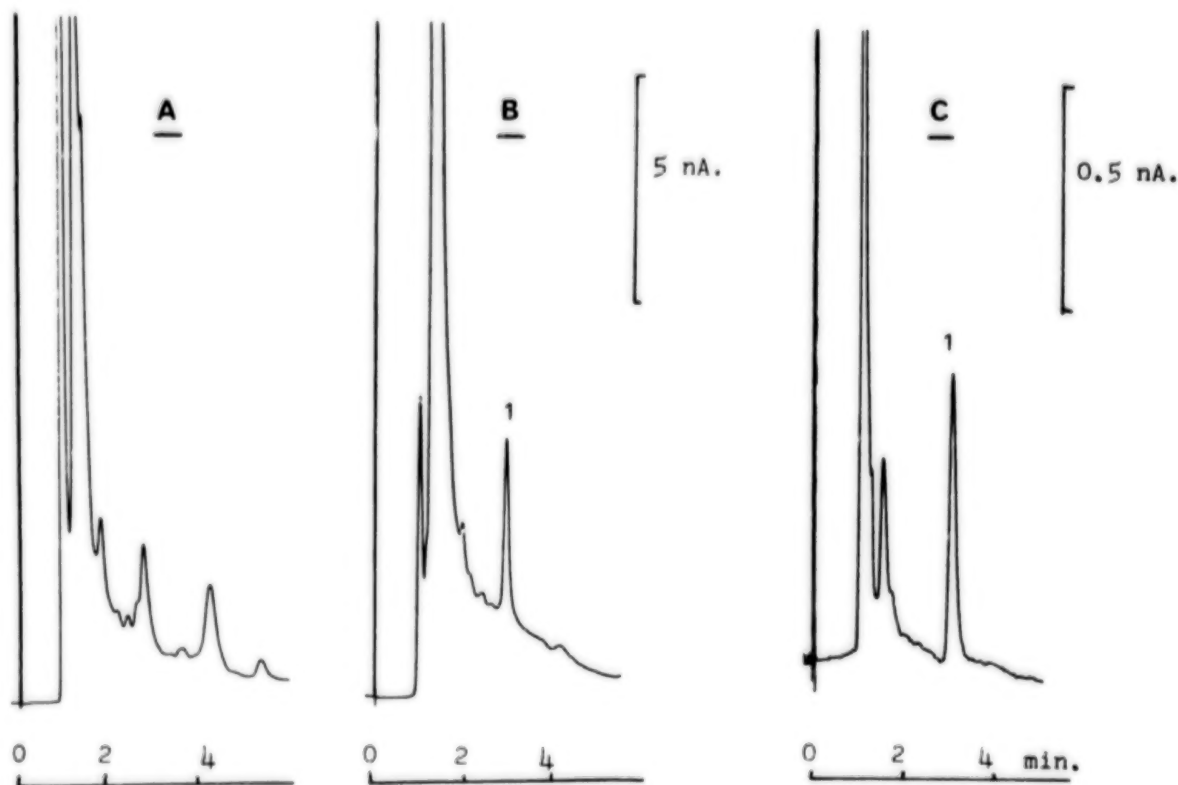


Figure 4. Diphenylamine (1) from clothes by HPLC using a reverse phase column, 65/35 methanol/water eluent and electrochemical detection at + 0.8 V. A-extract from a blank wool sweater ( $\frac{1}{2}$  sample injected). B-wool sweater 6 hours after firing 5 rounds of Winchester and Western Magnum .357 ammunition from the Model 19 revolver. C-5 ng/ml DPA standard in eluent (= 100 pg injected). Other conditions as in text.



Trials in which the subjects fired one day and were sampled the next produced no GSR, whereas GSR was readily detectable the next day on a jumper which had been removed immediately after firing and stored undisturbed. These results imply that the residue is lost by physical disturbance rather than by any chemical degradation. To confirm this cotton sheets were seeded with GSR by holding them one meter from the side of the revolver while five rounds were fired. The sheets were then stored undisturbed and were sampled periodically to check the level of GSR remaining; significant quantities of GSR were still detectable two months after the firing experiment.

### CONCLUSIONS

The work reported here was carried out in order to investigate the possibility of using the presence of organic GSR to provide evidence of a suspect's connection with the discharge of a firearm. The detection of organic GSR is potentially more useful than inorganic residue analysis by AAS or NAA. The analysis can be equally rapid and no problem should be encountered with environmental levels.

The work is at a very early stage and much more needs to be done in order to determine the nature, origin and persistence of the residues. However, the results so far show that the detection of organic GSR is a very promising area for further investigation. NG can be detected on hands two hours after firing a revolver but the sensitivity and hence the usefulness of the technique is limited by the lack of selectivity of the GC/ECD method. NG, DPA and NC can all be detected on clothes for a significant period after firing and it is likely that we will be applying this determination in the near future to casework samples as a screen prior to SEM analysis.

Before this is a possibility a number of advances in the technique of organic analysis must be made. We need a more selective method for NG detection. GC-MS using negative ion chemical ionisation or GC coupled to a Thermal Energy Analyser are the logical possibilities.

We also need an improved method of NC analysis. Size exclusion chromatography with reductive mode electrochemical detection should provide this.

These improvements are applications of existing proven methods, rather than fundamental new developments, and it is easy to predict therefore that

organic GSR analysis will find increasing use in the near future.

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## NEW MEASUREMENT STUDIES ON THE EFFECTS OF THE IEDS

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**ABSTRACT.** As in other countries, attacks by improvised explosive devices (IEDs) in the scene of politically motivated crime play an important role in FRG, too. The right assessment of their effects is of great importance both in order to ward off danger and from a forensic point of view. Indeed, everywhere attempts are made to answer this question by comparative blastings but mostly the appropriate methods are not available to obtain really evident and comparable measuring results. Therefore, at Bundeskriminalamt (BKA) methods of investigation have been established which can furnish (in a scientific sense) objective measurement data on the effects of IEDs. Measurement methods and apparatus for the experimental detection of the blast and fragmentation effects of IEDs are described since they are the most hazardous for human beings. The problems of providing conditions for carrying out suitable studies on explosion effects by means of comparative blastings are discussed. Exemplary measurement results and their conclusions are presented.

### INTRODUCTION

First, the following should be premised: If there is discussion about new measurement studies, it only means that the application of such studies, as they are reported here, is new to the field of criminal investigation, and new to IEDs (improvised explosive devices) as objects. The methods themselves are not new at all, since they have been applied for a very long time to the field of testing new weapons for military use. This fact, on the other hand, implies that only IEDs should be studied by those means; for, the complete data of the effects and performance of commercial and military explosives and of all kinds of weapons are already available. In those cases, the corresponding tables should be used and calculations should be made before carrying out large-scale experiments.

The aim in the case of measurement studies on the effects of IEDs is to get data that fulfill the following conditions:

- They must be comparable with the usual classification data of military weapons (bombs, war heads etc.).
- They must be obtained in a clearly defined

manner, concerning both the objects and the measurement methods. This means any team of technicians must be in a position to reproduce the results.

We want to achieve some method of characterising the effects of IEDs by numerical values which would render unnecessary any dependence on unsuitable descriptions in words. If we are successful with our project the courts will be provided with a better basis for judging offences committed in connection with IEDs. And, on the other hand, the police, in particular bomb technicians, will dispose of better facilities for estimating the hazards of IEDs. We have restricted our studies to the explosion effects on human beings, and we have only considered the effects of blast pressure and fragmentation, since they are the most important ones.

### PHYSICAL BASIS

Below, a brief review of the physical processes is given that occur when an IED explodes. We are not dealing here with detonating high explosives—for their behavior and effects are well known—but we must examine the improvised, "home-made" mixtures, which cannot normally detonate. Their reaction is just deflagration, and therefore bombs

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Table 1. PHYSIOLOGICAL EFFECTS OF BLAST OVERPRESSURE ON HUMAN BEINGS

effects	overpressure (norm. refl.)			
	short duration ( $<3$ ms)		long duration ( $>3$ ms)	
	bar	psi	bar	psi
eardrum failure				
threshold (1 percent)	0.35	5	0.2	3
50 percent	1.0	14.5	0.45	6.5
90 percent	—	—	0.85	12
lung damage				
threshold (1 percent)	2.5	36	1.0	14.5
50 percent	3.5	51	1.5	22
90 percent	5.5	80	2.0	29

charged with these mixtures require a strong metallic container wall. After ignition—there is no need of a detonator—the increasing internal gas pressure destroys the container, and by the sudden pressure jump at this moment an air blast wave is created. This shock wave propagates faster than the fumes and causes a long-range effect of the explosion. By contrast, the pressure of the fumes, *i.e.*, the overpressure of the gases originating from the solid (or liquid) explosive, constitutes a short-range effect. The waveform of the air-blast pressure looks as shown in Figure 1. This is the time-varying pressure, which is observed in a fixed place at a certain distance from the explosion center. The pressure jumps straight to its maximum value when the wave front arrives, but decreases more slowly and passes through a slight but long-lasting vacuum range before equalizing to normal atmospheric pressure. The decisive quantities for the physiological effects of the blast wave are the maximum pressure as well as the duration of the positive pulse. This is indicated in Table 1 where a distinction is made between injuries caused by exposure to short and to long pressure duration. The limit between “short” and “long” should be assumed to be a value of about 3 milliseconds.

It may be taken from these empiric results, which have their origin in the relevant literature (Cohen, 1968, Diephold *et al.* 1970, Jensen 1972), that exposure to long-lasting pressure causes more serious injuries at the same maximum value than exposure to pulse-like pressure. This implies that care must be taken in measurements to record both quantities, the maximum overpressure and the pulse length.

As mentioned before, the fragmentation effects

are at least as important as the blast wave effects. Since home-made explosives normally need the metallic confinement, fragments must be expected. The probability of their causing injuries can be correlated with their kinetic energy. It is a good approximation, if we assume that the threshold value for lethal injuries is about 80 Joules (which corresponds to 60 ft.-lb.). Therefore, in military language, fragments with a higher energy than this value are called “effective fragments” (French and Callender, 1962, Heiser, 1974). The measurement method of this threshold, as pointed out below, represents a simplified possibility for the detection of the fragmentation effects.

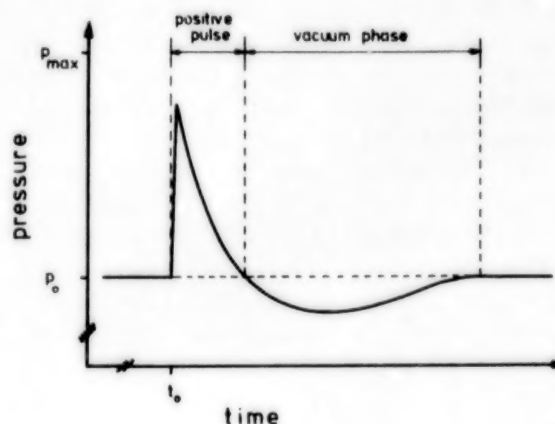


Figure 1. Schematic waveform of air blast pressure.

## EXPERIMENTAL

Below, the experimental setup for the detection of the blast wave and the fragment energy is described.

First, the blast wave measurement! As men-

tioned before, it is important to get the information on the maximum pressure as well as on the pulse duration. This means that the entire time-varying pressure curve must be detected. The suitable probes for this task are piezoelectric pressure transducers. Modern quartz transducers with built-in amplifiers as shown in Figure 2, offer a lot of advantages:

- high linearity over a wide range,
- high resonance frequency and
- high level voltage output at low output impedance, which allows the use in moist or dirty field environments.



Figure 2. Piezoelectric pressure transducer with built-in amplifier.

Their electric signals can be registered in a digital storing transient recorder and read out to a long-time store, for example a magnetic tape or a floppy disk. This enables all the further possibilities of computer analysis of measurement data. The schematic setup for a pressure detection experiment is shown in Figure 3. Several pressure probes containing the quartz transducers are positioned around the explosion center in different directions and distances, in order to furnish information on the local variation of the pressure. The electric signals are registered in the parallel channels of a transient recorder. For preliminary field analysis, a display unit is connected to make the curves visible. For the final computer analysis, the data are stored in a magnetic tape recorder.

The main problem in using quartz transducers consists in mounting these correctly in a pressure probe. Care must be taken that the transducer is mounted in such a way that the pressure detected is clearly defined physically. The pressure in a free

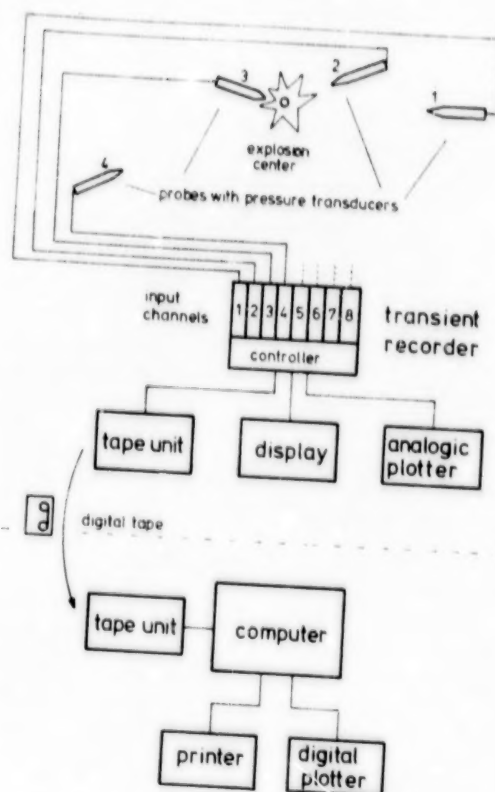


Figure 3. Total setup for blast pressure detection.

shock wave can be detected as shown in Figure 4. The transducer is perpendicular to the movement direction of the wave front and receives information on the "static pressure". The special shape of the probe with the peak pointed towards the explosion center prevents perturbation of the wave front, and thus wrong measurement. Besides, this setup represents effective protection from damage by fragment impacts. For the correct detection of the reflected pressure, the transducer must be inte-

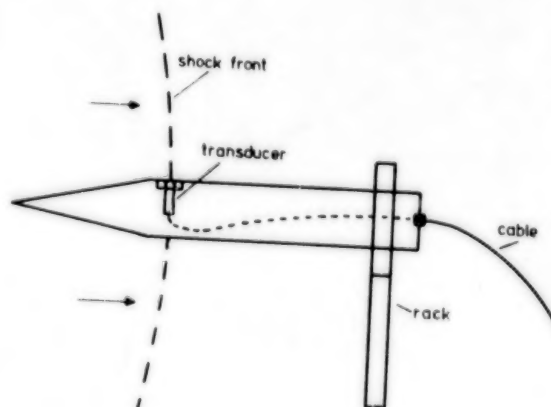


Figure 4. Pressure probe for the detection of static pressure in a free shock wave (schematically).



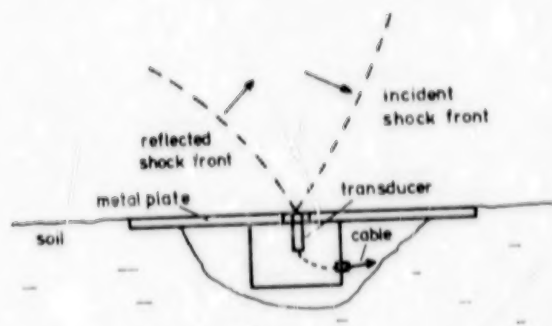


Figure 5. Pressure probe for the detection of reflected pressure (schematically).

grated in a plane metal plate, as shown schematically in Figure 5.

As mentioned before, there is a simplified method of detecting the fragment energy without using an expensive and sophisticated method such as X-ray flash photography. Since the kinetic energy of a fragment corresponds to its capability of penetrating a certain material of a certain thickness, and threshold energy may easily be measured by using one specific target material. Due to the quoted definition of "effective fragments", the

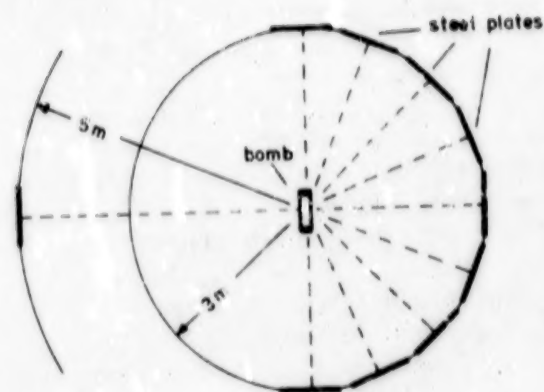


Figure 6. Schematic setup of a simplified "fragmentation garden".

important threshold of 80 Joules may be found out with the help of steel plates of a thickness of 1.5 mm. The experimental setup is called a "fragmentation garden". The plates are positioned in a certain manner around the IED, so that information may be obtained on the fragmentation hazards in different directions and at varying distances. We have used several simplified setups, for example, the one shown schematically in Figure 6. Figure 7 and Figure 8 show this fragmentation



Figure 7. Fragmentation garden before a test explosion.



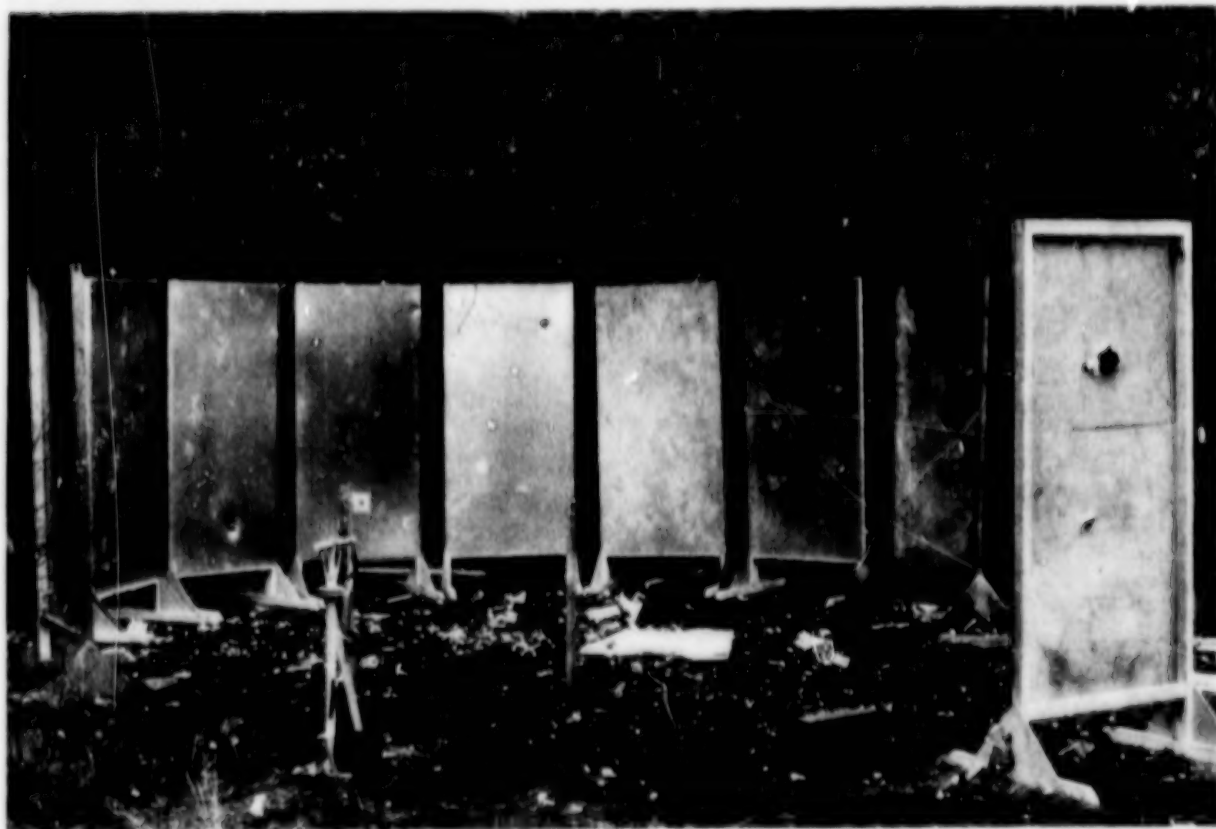


Figure 8. Fragmentation garden after a test explosion.

garden in practical use before and after a test explosion. The advantage of this fragmentation garden method is that it furnishes the distribution of lethal fragments in dependence on direction and distance, and besides leaves a very clear picture.

To complete the fragmentation analysis we need to establish the so called "fragmentation pattern". For this purpose, all fragments must be recovered by means of an IED explosion under sand

or under water (Figure 9). It is important to provide for an air environment of the bomb, so that natural fragmentation is rendered possible without direct confinement by sand or water. Figure 10 shows a typical fragmentation pattern of a pipe bomb that was filled with a home-made improvised explosive. The total number of fragments is smaller than in the case of a highly explosive charge. The mass distribution of the fragments is usually summarized in a diagram (Figure 11), where the number of fragments is plotted against their mass.

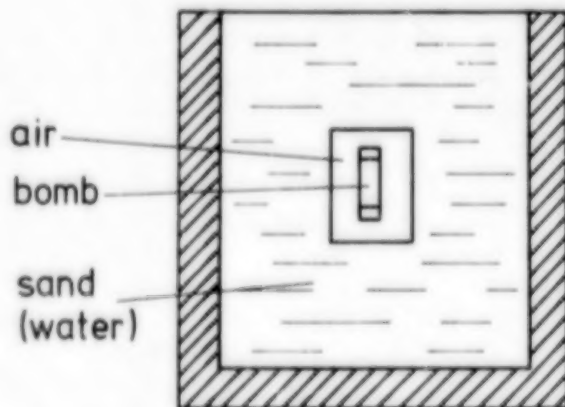


Figure 9. Schematic setup for fragment recovery.

#### Discussion About the Application of These Methods

The methods described just now may be applied to two investigation fields: To actual cases or to systematic research on IED effects. The prior condition for carrying out such studies in actual cases is the complete knowledge of the IED construction. The exact details of the container (its material, size, thickness), of the charge (its composition, particle sizes, quality of mixture) and of the ignition must be known. Otherwise, any experimental results by comparative blastings with



Figure 10. Fragmentation pattern of an IED (double walled pipe bomb).

reconstructed bombs are irrelevant and worthless. This must be considered especially in those cases where only information on the explosive residues is available. On the other hand, the great expenses of these studies mean a restriction of their applica-

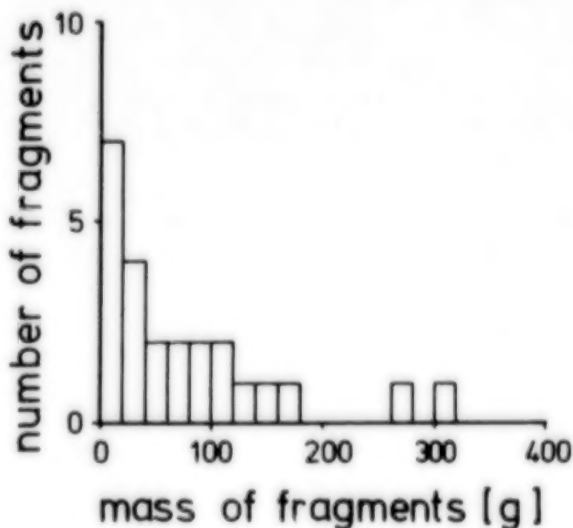


Figure 11. Fragment mass distribution diagram (corresponding to the fragmentation pattern of fig. 10).

tion on just the very important cases.

More significant results should be expected from systematic studies on the effects of IEDs. It is our aim to get the relevant information on the most frequent types of IEDs. For that purpose, we have started a series of investigations which, however, is restricted to a few idealized bomb types. The mixture ratio of the charges has been varied and different types of ignition have been used. Each experiment has to be repeated several times in order to provide for statistic safety. While carrying out this long-term program which may take several years, we are going to publish the individual results for use in the police field.

#### EXEMPLARY RESULTS

Below, some examples of experimental results and their conclusions are presented. First let us consider the application to actual cases! In the first example, a pipe bomb filled with a pyrotechnical flash mixture and a small quantity of an added propellant was investigated. Several specimens of the IED, secured in a terrorist apartment, were reconstructed (Figure 12). The wave-

Table 2. DISTRIBUTION OF EFFECTIVE FRAGMENTS IN EXAMPLE 1.

distance direction		2m	2m	2m	3m	3m	5m
		90°	45°	0°	45°	90°	0°
effective	1.	3	0	4	0	2	4
fragments	2.	2	0	5	0	4	4

form of the pressure curve, detected at a distance of 4 m from the explosion center is shown in Figure 13. The duration of the pressure pulse is shorter than 3 ms, which means that it shows the same time behavior as the blast wave of a high explosive of the corresponding charge weight. The maximum value of about 0.5 bar indicates that at this distance range the probability of eardrum failure is about 10 percent. Since this was our first investigation and we had not yet got the complete equipment, we did not study the pressure at various shorter distances. An estimative calculation furnished the pressure threshold of 2.5 bar for (fatal) lung damage at about 1.5 m distance. The results of fragmentation garden experiments are shown in Table 2. Effective (lethal) fragments were detected at all distance ranges investigated,

but there was a significant direction dependence of fragment distribution with maxima in, and perpendicular to, the axis of the pipe and minima in all 45 degree directions. A fragmentation pattern and a fragment mass distribution diagram of this IED are shown in Figure 10 and 11.

In the next example an IED consisting of a military handgrenade (type MK 2) with an improvised charge of 30 g of a propellant was to be investigated. There were only weak pressure effects (about 0.5 bar at 1 m distance and <0.1 bar at 2 m distance) but effective fragments could be detected up to a distance of 4 m. The fragmentation pattern (Figure 14) shows, that not all the predetermined breaking points were ruptured. Of course, this IED is not as hazardous as a military handgrenade with a highly explosive charge, but neverthe-

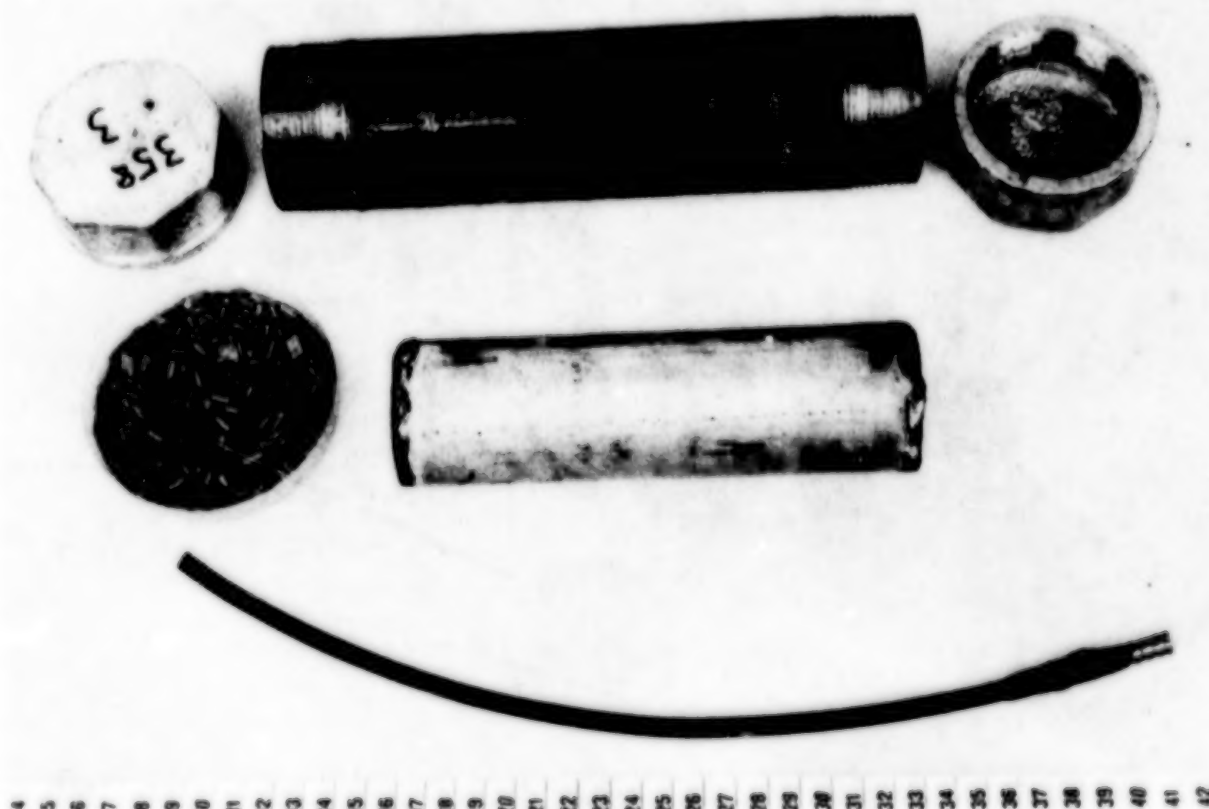


Figure 12. Construction of the IED in example 1.

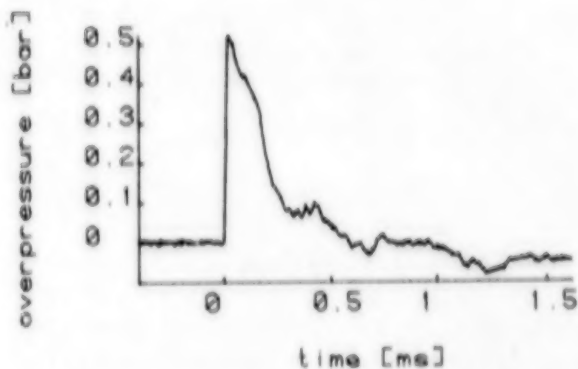


Figure 13. Overpressure waveform of the IED in example 1.

less it cannot be called harmless, either.

The object of the third example was a home-made firecracker which was composed of a lot of charges of smaller commercial pyrotechnical articles. As a confinement there was only aluminum foil and adhesive tape so that no fragmentation was to be expected. However, the pressure effects were considerable. Figure 15 shows the curve detected at a distance of 3m, which again represents the same time behavior as the blast wave of a high explosive of the corresponding charge weight. The maximum values of the static pressure in the free shock front (without reflection) were about 0.6



Figure 14. Fragmentation pattern of the IED in example 2.

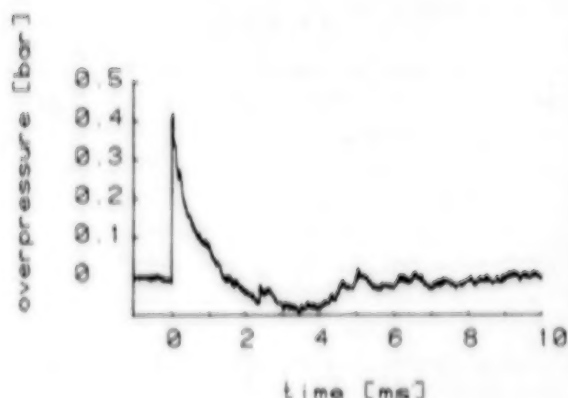


Figure 15. Overpressure waveform of the IED in example 3.

bar at a distance of 1 m and  $> 2.5$  bar at a distance of 0.5 m. This implies that the possibility of lung damage with fatal consequences in the short-range area cannot be excluded.

Finally, some preliminary results of the first series of systematic research on IED effects will be presented. As a first kind of idealized bomb container we have chosen 2-inch seamless water pipes of 25 cm length with two screw caps. The first mixture we have been studying is a very common home-made explosive in the German crime scene. It consists of a herbicide, containing sodium chlorate with 25 percent sodium chloride, and of sugar. The ratio we have been using first is 3.5 parts of the herbicide with 1 part of sugar, which represents nearly the ideal stoichiometric composition. Figure 16 shows a test IED just before blasting. The interruption of the wire around the pipe gives an electric pulse which is used for triggering the transient recorder. In this way we get the intermediate blast wave velocity till its arrival at the first pressure transducer. The results, we have obtained from this object are summarized as follows. Table 3 shows the intermediate values of the number of effective fragments and of the maximum overpressure, corrected for normal reflection. It can be taken from this table that there is no significant influence of the different ignition systems on fragmentation or blast effects, with one exception which surprises at first: The blast wave of the IED with the booster charge is much weaker than in the other cases. The reason is that the high order detonation of the booster destroys the container wall, before the whole improvised mixture comes to reaction. The local variation of the overpressure (Figure 17) corresponds to these above mentioned results. Besides, the weak effects of the moist charges, incidentally detected because of rainy weather, are not surprising.

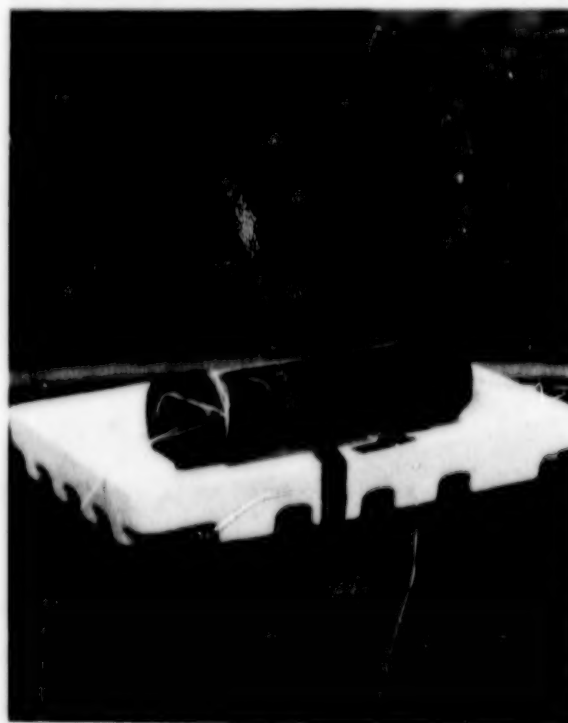


Figure 16. Test IED (pipe bomb) just before blasting.

Figure 18 shows the fragmentation distribution of this experimental series. In accordance with the geometry of the pipe bomb, there are three maxima of the fragmentation density: a broad one, perpendicular to the axis, and two sharper ones in prolongation of it. The minimum of the fragmentation probability of this kind of pipe bomb can be assumed at an angle of 30 degrees to the axis.

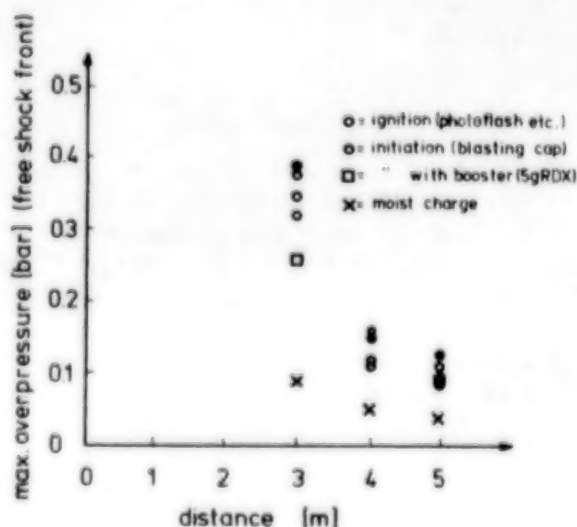


Figure 17. Local variation of maximum overpressure of the test series with chlorate/sugar charged pipe bombs.



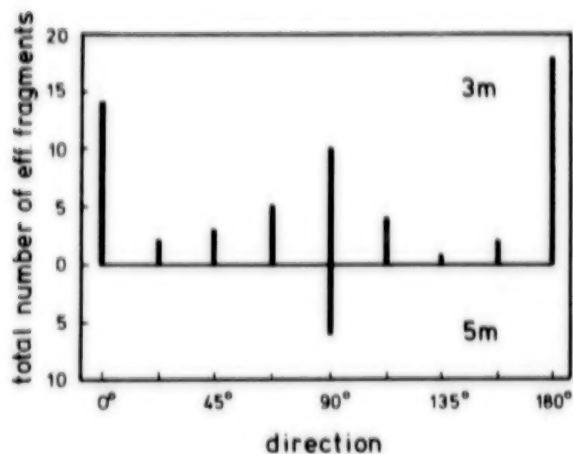


Figure 18. Fragmentation distribution of the test series with chlorate/sugar charged pipe bombs.

Table 3. INTERMEDIATE VALUES OF THE NUMBER OF EFFECTIVE FRAGMENTS AND THE MAXIMUM OVERPRESSURE OF THE TEST SERIES WITH CHLORATE/SUGAR CHARGED PIPE BOMBS

ignition system	effective fragments per explosion (3m distance, 10% sphere)	max. overpressure (3m distance, norm. reflected)	
		bar	psi
photoflash	3.5	0.64	9.3
gas lighter (wire bridge)	4.0	0.74	10.7
fuse head	2.5	0.70	10.2
blasting cap	3.25	0.78	11.3
blasting cap with booster (5g RDX)	3.0	0.52	7.5
[moist charge]	[0.5]	[0.18]	[2.6]

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## SUMMARY

At Bundeskriminalamt (BKA) methods of investigation have been established which can furnish (in a scientific sense) objective measurement data on the effects of IEDs (improvised explosive devices) on human beings.

Measurement methods and apparatus for the experimental detection of the blast wave and fragmentation effects of IEDs are described. The problems of providing conditions for carrying out suitable studies on explosion effects by means of comparative blastings are discussed. Exemplary measurement results and their conclusions are presented.

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## HIGH SPEED PHOTOGRAPHY OF CLANDESTINE EXPLOSIVE DEVICES

*Paul M. Dougherty*

San Mateo County Forensic Laboratories

A motion picture film made in the early 1970's, illustrated the effectiveness of high speed motion picture photography in the study of Clandestine devices. The contents of the film are shown at two different speeds; first at 64 fps, then at any speed from 600 fps to 4,800 fps, depending on the event.

The events are as follows:

1. Cherry bomb with BB (steel) glued to the sides. These were described in the late sixties for use in San Francisco against police.
2. Cherry bomb with tacks glued to sides. Again, these were described as used in San Francisco in the late sixties.
3. Bomb made of 2" x 6" water pipe filled with black powder.
4. Plastic garbage bag with approximately 1 gallon of gasoline then wrapped with several feet of detonating cord. This device was reported to have been used in a house in the Seattle, Washington area but this could not be confirmed at that time. The idea was to rig this device to the center of a room, and when the light switch was turned on the resulting fireball would envelope and kill who was ever in the room.
5. Homemade Napalm bomb using gasoline and Fels Naptha soap. This was initiated by a small explosive charge placed on the side of the bottle. The flame front's propagation in the gasoline vapor was clearly shown as was the spread of the liquid materials. This device was used in Berkeley in the late sixties or early seventies.
6. and 7. These were essentially the same device, champagne bottle base packed with C-4 to form a shape charge. In (7) the jet from the shape charge can be clearly seen on the other side of the target (*i.e.*, car door). Even with these crude materials and no stand-off an effective shape charge can be formed. Explosives other than C-4 may be used effectively.
8. Pipe bomb, 2" x 6", which was somewhat a

repeat of (3). The ground shock wave was clearly visible in this case.

9. Ammonium nitrate and diesel oil 95:5 by weight in a coffee can. The shock wave on the ground was visible. Also noted was the type of fireball created and the color of the smoke.
10. Telephone pole cut by a C-4 charge. Very high velocity type of explosion.
11. DuPont Jet (shape) Charge used to penetrate the sides of oil well casings. The detonation of the Primacord was shown in contact with the jet charge.

The following slides were taken as part of an on going study on Bomb debris, funded by the California Council on Criminal Justice (Project #0424). These were taken on February 27, 1973, for the purpose of added diagnostics regarding the reaction history of pipe bombs.

While two pipe bomb sets were shown, the pictures from one are being printed as typical of the series. Photographs are taken from 35 mm slides which are frames from a Model 189, Beckman and Whitley rotating mirror framing camera. Detonation velocity over the pipe was different for three locations on the pipe. This is believed to be due to non-uniform pipe wall thickness and non-uniform explosive loading density.

Photograph 1 illustrates the overall set-up to photograph at high speed the pipe bomb which is in the center of the picture at (A). Above and below it are lights for illumination, these are destroyed by the explosion. The wire entering the bomb goes to the SE-1 detonator which is near the center of the pipe bomb. The Series shown in 395F which consists of a 2" diameter 10" length schedule 40 welded wrought iron pipe with 369 grams of Bullseye powder (double base) Det. velocity measured was  $3.9 \pm .4$  MM/usec. The detonator used was an SE1 (high voltage) with Tetryl Pellet.\*

\* All photographs in this paper were taken at Lawrence Livermore Laboratory, Livermore, CA. and the author wishes to thank Mr. Charles A. Honodel and staff for their assistance.



Figure 1.



Figure 2. Time = 8 usec.



Figure 3. Time = 16 usec.



Figure 4. 24 usec.



Figure 5. Time = 32 usec.

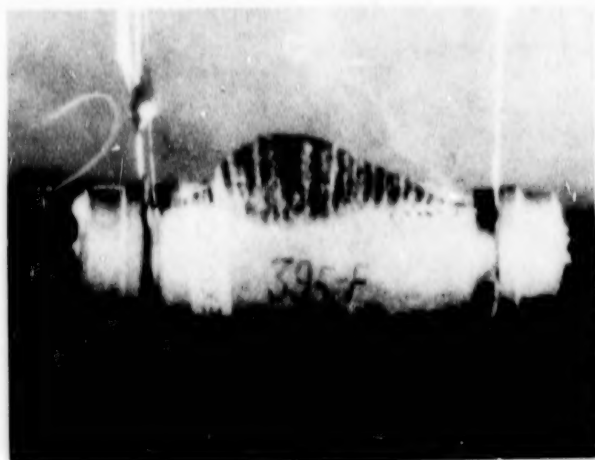


Figure 6. Time 40 usec.



Figure 7. Time = 56 usec.

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# DETECTION OF IMPROVISED EXPLOSIVE DEVICES A SYSTEM FOR ENSURING MAIL SAFETY

Authors: *D. W. Williams, K.K.M. Wu, S. R. Silva and J. D. Quinn*

## 1. BACKGROUND

The research and development program of the Materials Research Laboratories on image recognition commenced with the request from the Australian Federal Police for scientific support in the area of combating terrorist activities. Of special concern to the Federal Police was the detection and recognition of improvised explosive devices (IED's), especially in the form of letter or packet bombs. A wide range of techniques were considered. These methods include those dependent upon vapour trace detection, atomic or nuclear properties, thermal or RF/microwave responses, X-ray transmission/fluorescence, electrical properties of explosives and on chemical or radioactive additives to explosives. It was concluded that the X-ray fluoroscopy technique was the most suitable. However, the recognition of an IED image depends upon the quality of an operator's observation and analysis. It is recognized that such dependency on human involvement is unsatisfactory for situations in which a large number of articles need to be cleared quickly, *i.e.* a high throughput situation. In this type of situation there is a need for rapid machine clearance of the bulk of innocuous articles, so that only a small percentage of suspect articles need to be examined by an operator, whose involvement would be required only when the machine's detection/recognition capability was exceeded.

After close examination of IED designs provided by the police, the Army, postal securities and those reported in terrorist literatures (*e.g.* "The Anarchist's Cookbook"), we came to the conclusion that a letter- or parcel- detonator (blasting cap) with its priming explosive initiator such as ASA (lead azide, lead styphnate, aluminum powder). The priming charge being of heavy metal salt has a high X-ray attenuation coefficient. In addition, an effective letter bomb must contain components, such as a battery or a mechanical striker, to provide the energy required for initiation of the detonator. These components usually also have high X-ray attenuation coefficients. The attenua-

tion of X-rays through such components effects image contrast on a fluorescent screen. Based on this knowledge, we have designed two systems, System I & II, to automatically screen the mail for letter-bombs at high speed.

The following description deals first with System I, second, with the operational results obtained at CHOGM\* using System I, and third with the development of System II.

## 2. SYSTEM I

The high volume mail bomb screening device (Figure 1) may be described schematically as comprising three main functional blocks; first the X-ray imaging system which produces an image on a fluorescent screen, second, the closed circuit television (CCTV) camera, and third, the Real Time Video Processor (RTVP) or System I.

### 2.1 Hardware

#### (a) X-ray Imaging System

The X-ray imaging system consists of an X-ray generator and an X-ray fluorescent screen. Two types of screen, a DuPont Cronex E2 screen covering an area of 250 x 250 mm and a Sirius HSF screen of 385 x 285 mm have been used successfully to date. The E2 screen is a fast response, high sensitivity type. However, it lacks image sharpness when compared to the slower Sirius HSF screen. The optimum choice of fluorescent screen is related to the area to be covered. X-ray energies of between 80 and 150 kV were the most suitable for IED detection, giving good contrast images and allowing safe operation.

A Silicon Intensified Target (SIT) CCTV camera is used to convert the optical image produced on the fluorescent screen to an electronic signal. The SIT CCTV camera has a bandwidth of 15 MHz and a line to line resolution of 500 lines.

#### (c) Real Time Video Processor

The technical description of the Real Time Vi-

\* Commonwealth Heads of Government Meeting Held in Melbourne 1981.

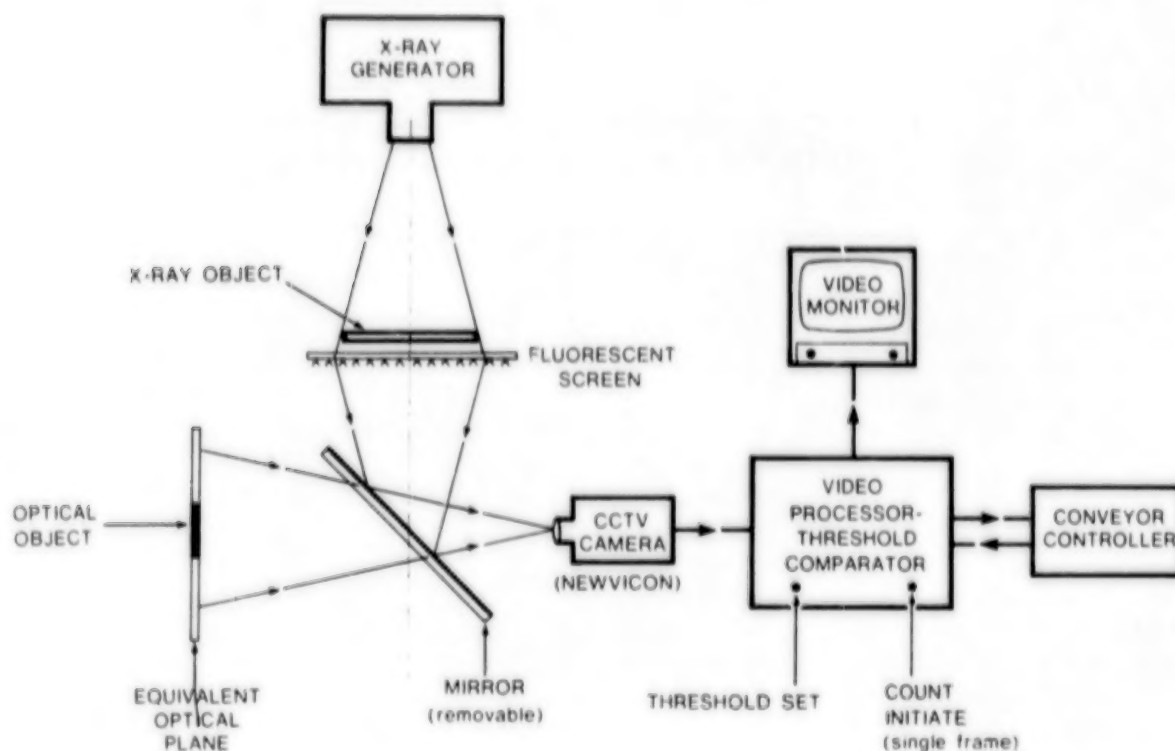


Figure 1. Schematic diagram of experimental system.

deo Processor, RTVP, is shown schematically in Figure 3. The Processor consists of six functional blocks, labelled 1 to 6 in Figure 2 as follows:

1. High speed video comparator and keyed clamp.
2. Window generator and clamp driver.
3. Double field counter.
4. Dark area counter and digital comparator.
5. Video synchronizing pulse separator and buffer, or Video synchronizing pulse generator.
6. Video mixer and selector.

## 2.2 Principle of Operation

A video signal from the CCTV camera is fed to the high speed comparator. The comparator level is adjustable by the operation of a multiturn potentiometer. The comparator, 1, output consists of a stream of information as the video level varies above and below the selected threshold level. When the video is darker than this preset threshold value an output signal, D, is produced (Figure 2).

A window generator, 2, activates the area counter in the selected area of the picture as viewed on the CCTV monitor. This monitored area is referred to as the "window". The size and

position of this window can be controlled by the operator.

Start signals, S, are fed to the double field counter, 3, from either the control input or a manual switch. The area count is zeroed, R, at this point. Enable signals are generated by this counter for the next two successive fields following either a manual or automatic start signal (*i.e.* one odd and one even (raster line) field to make a complete frame).

The dark area counter and comparator, 4, is activated only when enable signals from the comparator, the window generator and the double field counter, F, W, & D, are presented to it simultaneously. While activated the area counter counts time intervals locally generated by a crystal clock and totalizes this count over a complete frame. This count is directly proportional to the CCTV picture area scanned when enable signals are present. A digital comparator then feeds the control ports indicating the status of the totalized count for the frame, *i.e.* above or below a present area limit. The operator is allowed prior selection of a count value above which he requires a control output to hold (or divert) the item, H. Control ports are provided for interfacing the start, and hold (or divert) signals, with automated handling equip-

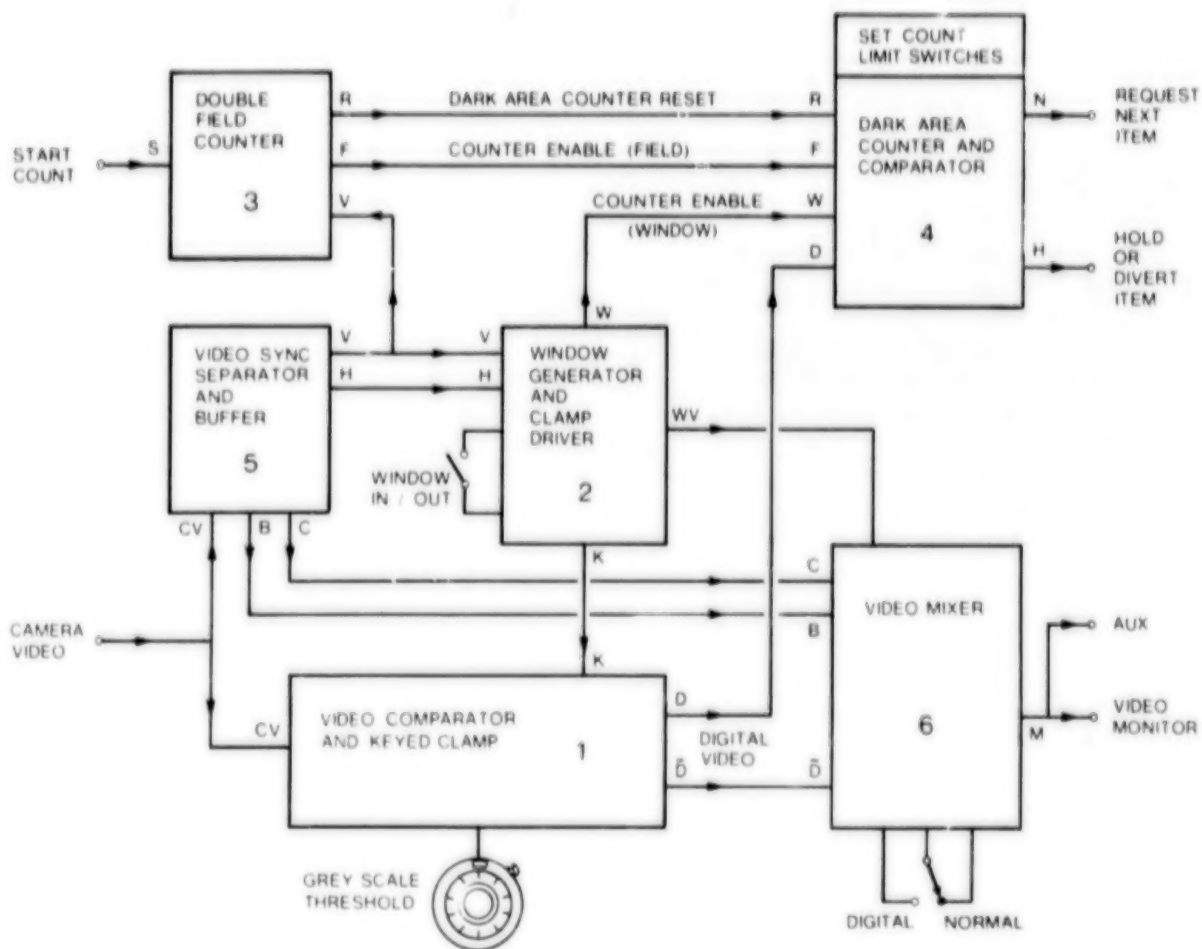


Figure 2. Schematic diagram of real time video processor.



Figure 3. Real time video processor.

ment for parcels, letters, etc.

Video synchronizing signals are required by the double field counter and the window generator. These are provided from either the synchronizing separator, 5, using the CCTV video, or by a synchronizing pulse generator acting as a master control for both the CCTV camera and the processor.

Signals from the video comparator, window generator, synchronizing signal, separator generator and input video buffer are fed to the video mixer to provide the following outputs:

- (a) Digital video (darker than the set threshold is shown black, remainder shown white).
- (b) Direct camera video (full grey scale).

The window area may be superimposed on either of the selected outputs which are displayed on the video monitor. A hold or divert signal is produced for an image containing areas darker than the preset grey level and producing counts greater than the preset area count.

To summarize: The composite output from the CCTV camera is fed to the comparator system. Operating at high speed the comparator provides an output signal for areas of the fluorescent screen which have luminance less than the preset (grey level) threshold. A window area of the fluorescent screen is selected to be analyzed, by virtue of command signals that are generated within the comparator.

The video monitor is able to be switched to display:

- (i) the CCTV camera video, or
- (ii) the comparator output

This switching displays the areas of the fluorescent screen which are darker than the preset threshold. For field operation it is proposed to provide the operator with a complete CCTV image (effectively of 512 lines of 512 pixels/line) of any item which fails to pass the test, and, if required, an alarm to draw attention of the operator to the unit. Within the selected area of the fluorescent screen the article being analysed is readily observed on the monitor. The relationship between counts and area depends upon the magnification factor of fluorescent screen image to CCTV image. The requirement is to scan a 300 mm x 400 mm image which should include the largest standard mail envelope of size 285 x 385 mm. Each count will then represent 0.5 mm<sup>2</sup> of such a field. Present limitations of the laboratory equipment allow a window size of only 300 x 100 mm. Increase of the window would involve the use of shade correction to improve image segmentation at the edge. The interconnec-

tion of RTVP with other modules is shown in Figure 4.

### 3. OPERATIONAL TRIAL AT CHOGM

System I was installed at the CHOGM mail security centre with the Australian Federal Police mail checking equipment which included a Line Scan System and a Torrex II Fluoroscopic Inspection System, both of the Scan Ray Corporation, and several vapour trace detectors (VTD).

#### 3.1 Procedures

Mail delivered by Australia Post was first examined by the Line Scan and, depending on whether identification was established, was followed by fluoroscopic and VTD checks. Further checks were carried out by System I. The Police equipment (apart from VTD's) required visual examination and image interpretation by observers trained in bomb recognition, whereas System I could clear or reject mail automatically.

#### 3.2 Mail Statistics

A total of nearly 8000 mail items was checked. The numbers and categories of items accepted or rejected by System I are given in Table 1. Rejection is on the basis of an X-ray density equal to or greater than that of a minimum size bomb which would be capable of causing significant injury (1). Rejected items are divided into two categories in the Table—Category A (non-stationery) consisting of miscellaneous articles such as corkscrews, scissors, keys, cassettes, etc.) and Category B items (stationery). Respective values as a percentage of total mail items are 0.6% and 1.8%.

System I controls were set to clear individual items at a ratio of two per second. This rate could be increased by an order of magnitude by the stacking of mail items. However, the clearance rate as set was more than adequate for the throughput involved.

The stop signal which interrupts the power supply to the conveyor belt motor was spuriously activated by electrical noise on three occasions. The origin of noise and its mode of propagation through the equipment was determined and the noise was subsequently eliminated.

#### 3.3 Detection of Concealed Objects

Shortly after the commencement of mail checking, it became apparent that Category A items could present a detection problem—the concealment, whether by accident or design, of an explosive device by an identifiable innocuous object of



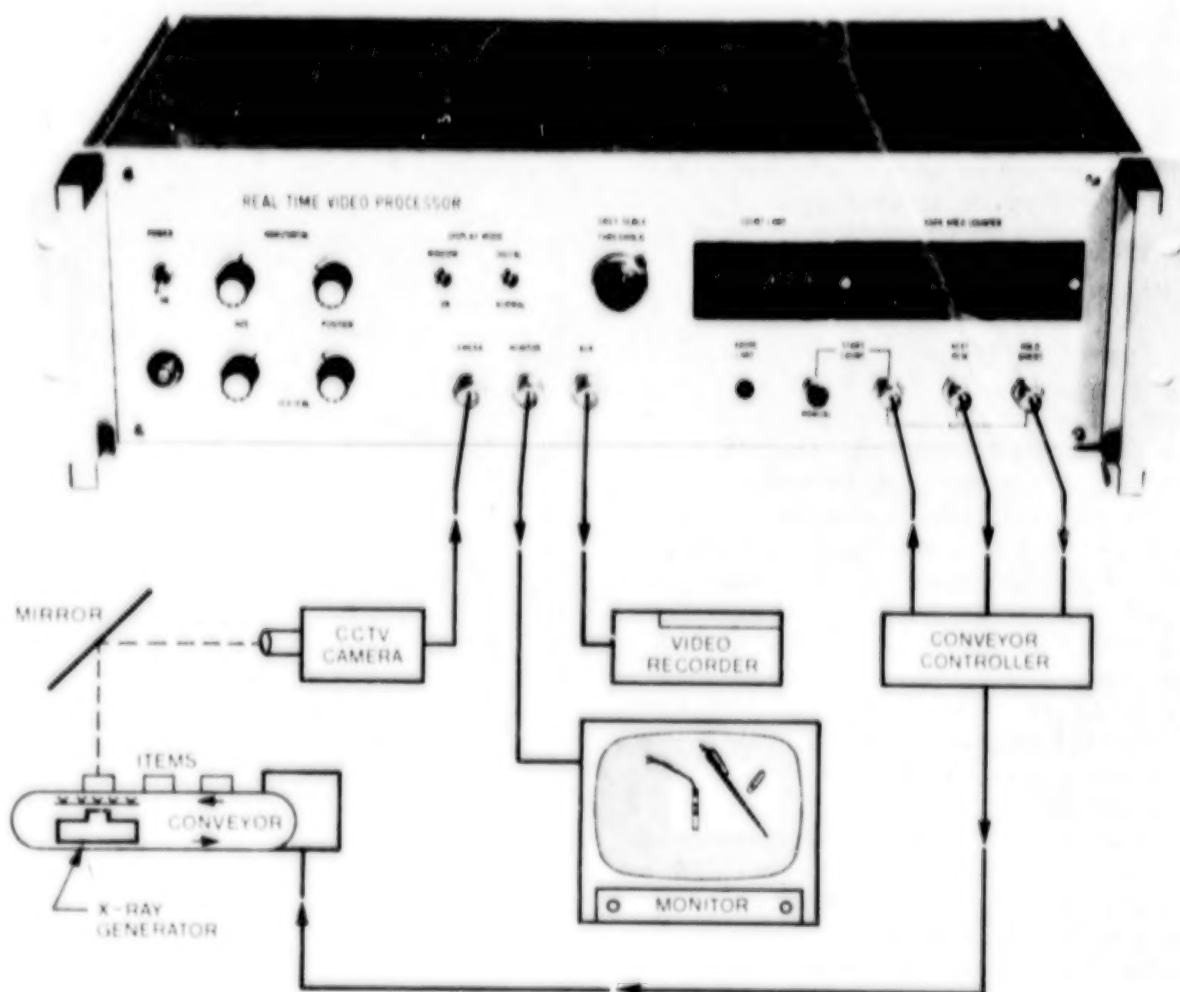


Figure 4. RTVP with layout for continuous monitoring.

Table 1. MAIL CLEARED OR REJECTED BY SYSTEM I

Description	Number	Percentage of total
Mail Processed	7824	100%
Mail Cleared	7634	97.6%
Mail Rejected (Category A)		
Miscellaneous articles	22	
Keys	24	
Cassettes	4	
Sub-total	50	0.6%
Mail Rejected (Category B)		
Stacks of letters	6	
Books and paper	44	
Paper Rolls and Staples	21	
Clips or fasteners	66	
noise	3	
Sub-Total	140	1.8%
TOTAL	190	2.4%

sufficient area and X-ray density. The capability of System I to display a binary image for a variable threshold may be varied to reveal intensity differences which cannot otherwise be discerned by human vision. To our knowledge no other system used for mail inspection has this capability.

### 3.4 Discussion of Results

Percentage clearance and rejection values given in Table 1 show that System I cleared 97.6% of mail free of IED's as safe. The system can therefore be regarded as a 'stand alone' system when employed in a mail registry situation handling up to a few thousand articles daily. The 2.4% of the mail which cannot be cleared by the system need then be examined fluoroscopically by an observer. However, in the case of a major mail exchange where the throughput requirement may reach 60,000 articles per hour, with a daily volume well exceeding one million, the small percentage of suspect articles would still amount to a large volume and need to be cleared at the rate of 1440 articles per hour in order to avoid serious back log.

Table 1 showed that the three quarters of the mail rejected by the System—1.8% of the total—contained various types of stationery items including large metal paper clips and paper fasteners (Category B). It is envisaged that these items may be automatically identified, and subsequently cleared, by a system with pattern recognition capability, leaving only the remainder, 0.6% of the mail (Category A), to an observer for further inspection. For a throughput rate of 60,000 articles per hour, this is equivalent to 360 articles per hour—a rate easily manageable by observers. It is therefore adjustable on the basis of these statistics to upgrade System I by incorporating a micro-processor to give the required pattern recognition capability.

An additional justification would be that of providing further capability in the recognition of a particular bomb design(s). This could be of advantage in the provision of quick response to a particular bomb threat by a known design through the insertion of parametric data into a recognition algorithm designed for this purpose. The upgraded system is known as System II.

### 4. SYSTEM II

Figure 5 is a schematic diagram showing the basic arrangement of equipment and the manner of linking the equipment to the multibus of the single board computer utilized for the purpose of carrying out the pattern recognition.

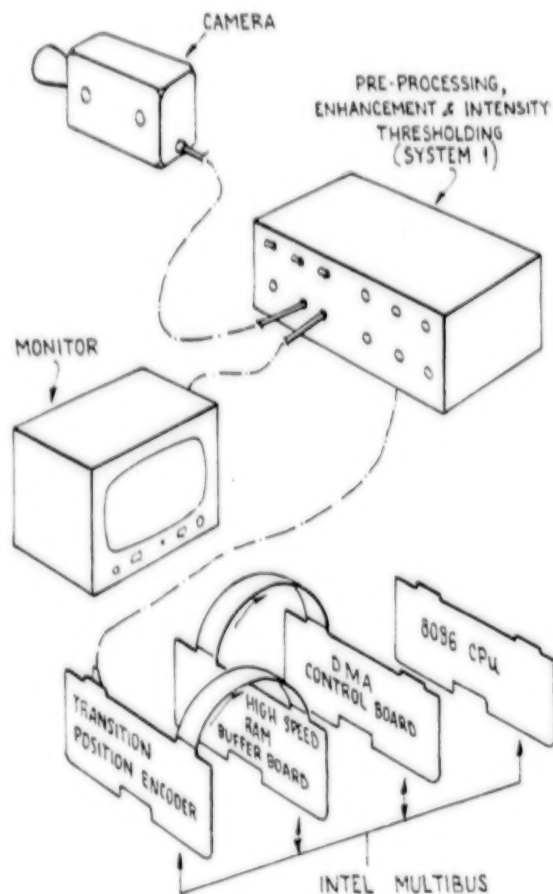


Figure 5. Schematic diagram of system II.

### 4.1 Image Acquisition

Figure 6 is a block diagram of the image acquisition system. The video signal from the CCTV camera is processed by the 'comparator' into binary data according to a preselected threshold intensity level as in System I. The output signal is then processed by the Encoder Board into run-end code data. The horizontal position of each transition, from white to black or vice versa, along a line during the raster scan is inserted into the word generated at the end of each line. Since the TV raster scan is composed of two consecutive interlaced field of 256 lines each, an image is thus recorded in the form of a 512 x 512 matrix.

A large reduction in the quantity of data to be stored, hence the overall data transfer rate, may be achieved through run-end coding. Nevertheless, each word is generated in a minimum time of 120 nanosecond and needs to be stored at this rate. This is handled by the High Speed RAM Buffer Board, which incorporates two identical high speed 1K x 1 word Intel-2115A static ram boards, in the manner described below.

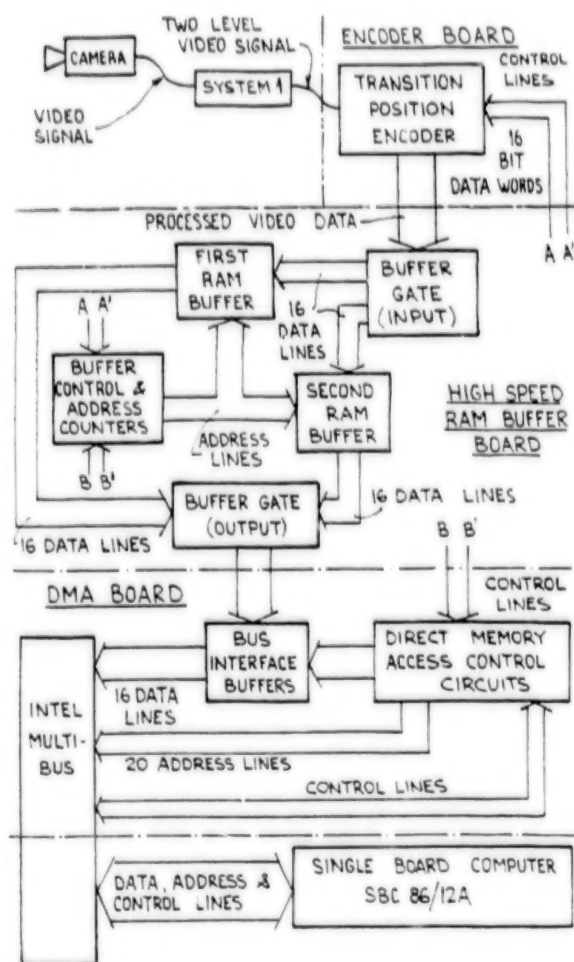


Figure 6. Block circuitry of the image acquisition system.

(1) As the data is generated, it flows into the First Buffer. When this is filled, the 16 bit data path is immediately switched to the input of the Second Buffer.

(2) In the same time as the data is flowing into the second Buffer, the data temporarily stored in the First Buffer is transferred by a direct memory access circuit to the memory of the central processing unit, an Intel 86/12 single board computer.

(3) When the Second Buffer is filled, the input data path is switched back to the First Buffer. By this time, the data in the First Buffer would have been emptied into the memory of the CPU.

(4) The process continues until the completion of the interlaced picture scan.

#### 4.2 Image Analysis

At the completion of data transfer, the 8086 microprocessor of the computer is activated to begin analysis of the image. The data of transition pairs are rearranged to form a 512 line single frame from the two 256 line half frames. Overlapping

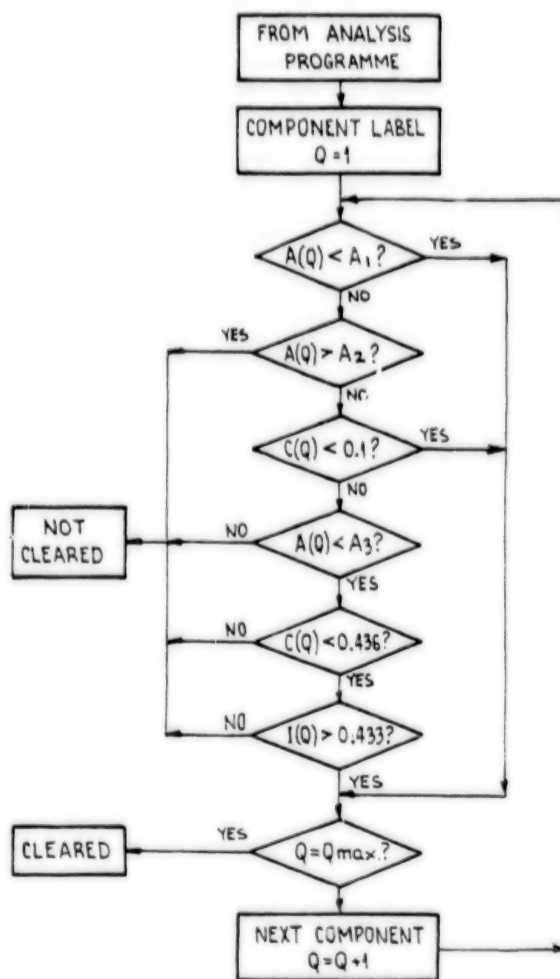


Figure 7. Algorithm for the clearance of paper clips.

pairs on successive lines are then grouped to form individual objects by a component labelling algorithm. The algorithm is based on that of run-tracking, which is particularly suitable for image data in run-end coded form. The runs are located sequentially from left to right along each line, each run is treated as belonging to a new object, thus given a new label. The labels which are usually whole numbers start with 1 then continue in ascending order according to the order in which the objects are encountered. On the second and subsequent lines, each run is subjected to an overlap search to determine whether it overlaps with any run on the preceding line. The run is assigned a new, hitherto unused label, if there is no overlap. But, if there is overlap, it is given the same label as the run it overlapped. The overlap search is continued to determine whether it also overlaps with the next run on the preceding line. If there is more overlap, and the runs are of different labels, the run with the higher number is relabelled with the lower number.

### 4.3 Feature measurement

The identification of objects is to be based on shape information independent of size and orientation. Geometrical features which are readily extracted from the image and which may be computed in a single pass during the labelling process are chosen. The more exotic shape descriptors such as the Fourier descriptor and differential chain code are not preferred because they would require images with well defined boundaries and would involve greater computational effort. The features we have computed include area, perimeter, moments about a fixed point, vertical and horizontal Feret diameter, and secondary features such as centroid, circularity and central moments.

### 4.4 Algorithm For Clearance of Paper Clips

The automatic mail clearance is referred to as IED detection. The automatic identification of letter bombs is extremely difficult if not impossible, since there is no standard bomb design. Although there may be essential bomb components such as a detonator and energy source, yet they come in various size, shape and are assembled differently. In addition to this, the probability of a letter containing IED is extremely low. Even if we can design a set of detection criterion to cover a wide range of IED configurations, the application of the criterion to every letter in search of virtually non-existent item is inefficient. The present strategy is to discriminate a limited variety of stationery items from other articles based on their geometrical features. The requirement is therefore to identify those characteristic features of these items which are not possessed by essential components of IED, *i.e.* the detonator and the energy source. Any mail containing items which cannot be cleared according to those features, must be treated as suspect and inspected by a human operator or by more sophisticated techniques.

A preliminary scheme for the clearance of mail containing paper clips is presented as an example in the flow chart of Figure 7. This basis of adopting each criterion is explained below:—

#### Criterion 1

Objects below a minimum size,  $A_1$ , may be disregarded. It is designed to eliminate noise and fragments of image close to the intensity threshold. The minimum size is chosen to be well below the size of items such as the priming charge of a detonator, blob of solder in electronic circuits, electric wire junctions, etc.

#### Criterion 2

Mail containing items over a maximum size,  $A_2$ , are not cleared.  $A_2$  is set to be the size of the largest paper clip designed to be cleared.

#### Criterion 3

All paper clips are characterized by a small value of circulatory,  $C$ , coupled with a large value of area normalised moment of inertia,  $I$ . In particular, the  $C$  of paper clips are much lower than those of compact items. Therefore, we may clear items with  $C$  below, say, 0.1 as paper clips.

#### Criterion 4

When the image of paper clips is fragmented through thresholding the  $C$  of fragmented parts can be greater than the value 0.1 used in Criterion 3. These fragments often appear as bar-like items with a length to width ratio,  $a/b$ , greater than 5. This corresponds to values  $C < 0.436$  and  $I > 0.433$ . Because the fragments are much narrower than other compact items with the same  $a/b$  ratio, their area counts are comparatively much lower. Thus, items of size below certain value,  $A_3$ , and with  $C < 0.436$  coupled with  $I > 0.433$ , may be cleared as fragments of paper clips.

The choice of quantities  $A_1$ ,  $A_2$ , and  $A_3$  appeared in the above criteria is dependent upon the exposure and threshold conditions, and should be subject to field trials.

### 4.5 Performance

At the time of reporting, System II has not been fully tested. The image acquisition system described in Section 4.1, however, has been tested. It can successfully store images in run-end code form in 1/25 second—two consecutive interlaced half TV frames. The image analysis algorithms have also been tested and proven. The speed of analysis is dependent upon the complexity of an image. It took an average of 5 seconds to analyse images with 1000 transition points using an LSI 11/2 processor with programmes written in Fortran. This speed could be increased at least five times on a faster 86/12A processor. Hence, System II could be capable of achieving a throughput rate of approximately 3600 articles per hour which exceeds the rate of 1440 articles per hour required for processing all mail rejected by System I in the mail exchange situation.

We have tried the clearance scheme (Section 4.4) on images of simulated mail containing various types of paper clips at several intensity threshold levels and on images of simulated IED

of the types detected by Australian and British postal authorities. The results indicated that paper clips could be cleared as safe in over 90% of the cases, whereas not a single IED component analyzed was cleared as safe.

### 5. SUMMARY

We have developed the basis for two systems for automatic screening of mail for letter bombs at high speed. The first system, System I, employs a closed circuit television camera for viewing the fluoroscopic image. The video signal from the camera is passed through a 'comparator' providing an output signal for regions of the fluorescent screen which are darker than a preselected intensity threshold. The output is then fed to the gate input of a counter/timer, which provides a measure of the total duration of the signal in one TV raster scan, indicating the extent of the darker areas of the image. A letter is cleared as being safe when the extent of the dark areas is less than a preselected threshold corresponding to the minimum size bomb considered to be effective.

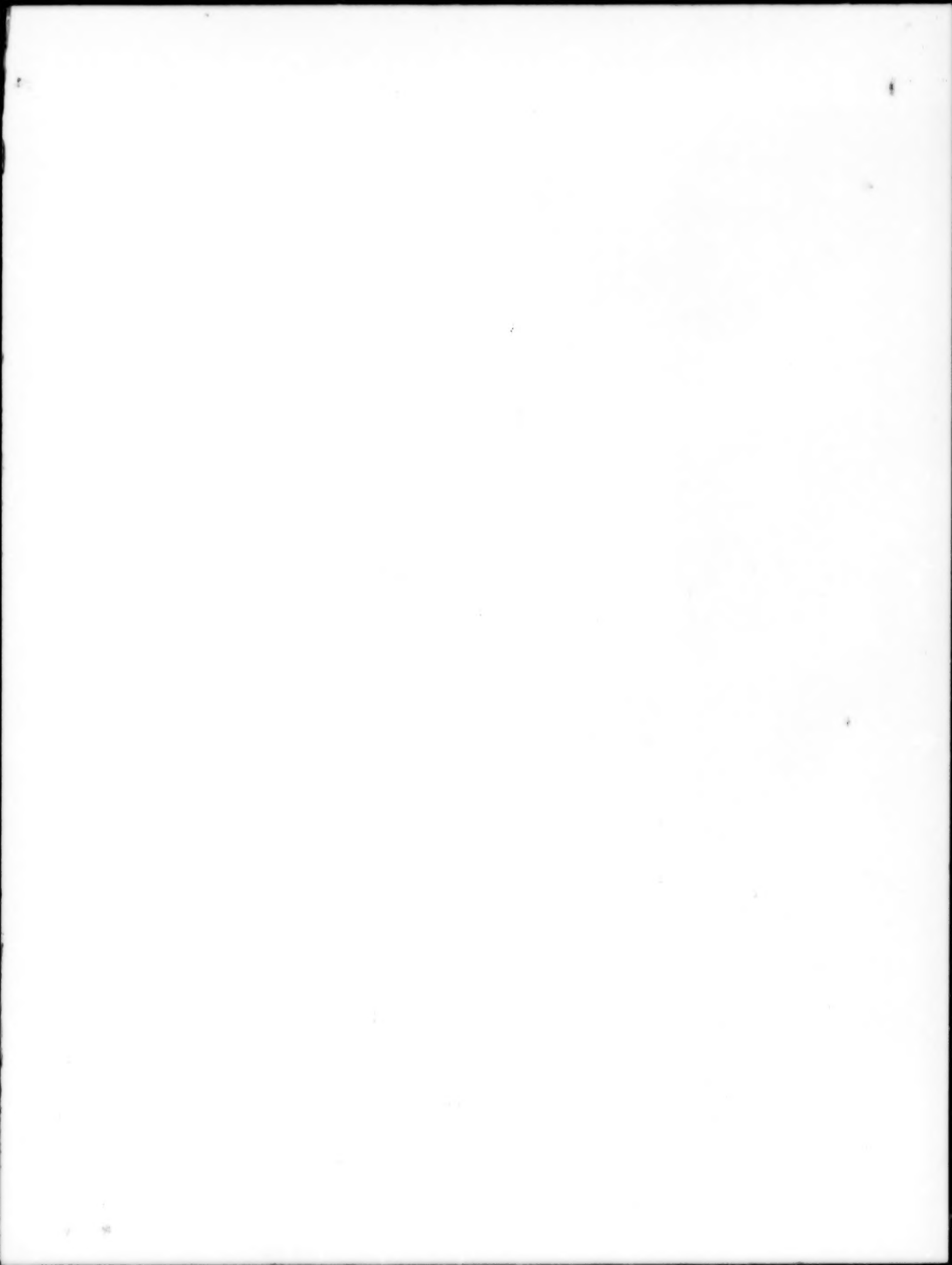
It has been established from trial at the CHOGM in Melbourne 1981, that 97.6% of the mail received contained only paper and small paper clips, pins and staples. It was possible to set the threshold levels of the system so as to clear these letters as being safe while rejecting without failure those containing as little as a single detonator as being unsafe. The system makes decisions in real time, however, a practical system will be limited by the throughput rate of the feeding mechanism. During the trial a rate of two items

per second was achieved with a simple conveyor belt. System I can be regarded as a 'stand alone' system when employed in a large mail Registry situation handling say up to 1000 articles daily. The 2.4% or so of the mail which cannot be cleared by the system may then be examined fluoroscopically by an observer.

A second system, System II, has been developed in experimental form to clear stationery items using pattern recognition techniques. It is essentially System I with the addition of a microprocessor, Intel 86/12 single board computer. The signal output from System I is processed by the Encoder Board into run-end code data, which is then stored in the CPU by High Speed RAM Buffer Board. The whole process takes 1/25 second, two half frames. The segmentation of images and the determination of geometrical attributes of the segmented objects may be achieved in approximately one second. System II has not been engineered fully or tested in an operational environment. However, we have tested a clearance scheme on images of various types of paper clips at several intensity threshold levels, and on images of simulated IED's. The scheme was capable of clearing paper clips as safe in over 90% of the cases, whereas it did not clear as safe a single IED component tested.

### REFERENCE

1. *Lidstone, D. P.* Letter Bombs: A guide for the layman Forensic Explosives Laboratory, R.A.R.D.E., Royal Arsenal East, London. Prepared 1972.





**END**

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